RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY—1938. Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W. 1, England. 7¼ x 9¾ in. 141 pp. Price to members, 2/6 (approximately 60c); to non-members, 10/6 (approximately $2.60).

This is the second issue of the annual reports being issued by the I.R.I. to keep its members and non-members abreast with developments in the field of rubber technology. As in the first number, developments in various branches of the industry—from planting to manufacturing—are reviewed by authorities in the respective fields. Complete bibliographical references are given at the end of each review. Author and subject indexes are included. The subjects covered, and the authors of each, follow herewith.

History, General and Miscellaneous, and Statistics, by J. P. Griffiths; *Planting and Production of Raw Rubber and Latex,* by J. Grantham; *Properties, Applications and Utilization of Latex, Including Treatment of Fabric with Latex,* by F. H. Cotton; *Raw Rubber,* by R. W. West; *Synthetic Rubber,* by W. J. S. Naunton; *Testing Equipment, General, and Specifications Other Than Latex,* by George Martin; *Compounding Ingredients, General, Vulcanizing Accelerators, Antioxidants and Softeners,* by W. J. S. Naunton; *Fabrics and Textiles,* by W. Knight.

Chemical and Physical Properties of Vulcanized Rubber, by R. W. West; *Tires,* by J. G. Mackay; *Belting,* by G. F. Payne; *Rubber Hose and Tubing,* by J. Kirkwood; *Cables and Electrical Insulation,* by C. J. Beaver; *Footwear,* by A. Johnston; *Games and Sport Accessories,* by J. G. Mackay; *Mechanical Rubber Goods,* by H. Rogers; *Roads,* by G. E. Coombs; *Rubber Flooring,* by A. W. F. Chatfield; *Surgical Goods,* by C. R. Pinnell; *Textile-Rubber Composites, Solvents, Cements,* by W. N. Lister; *Sponge Rubber,* by J. D. Campbell; *Hard Rubber,* by H. A. Daynes; *Works Processes, Materials, Including the Treatment of Raw Rubber in the Factory, and the Treatment of Vulcanized Rubber,* by B. L. Davies; *Machinery and Appliances,* by Colin Macbeth. [From *The Rubber Age* of New York.]

THE FIRST REPORT OF THE RUBBER FOUNDATION 1936-37. Rubber Stichting, Heerengracht 182, Amsterdam, Holland. 124 pages.

This report covers the period from October 31, 1936, when the foundation was established, to December 31, 1937, and gives information regarding the formation of this organization, the board, delegates, committees, etc., and the various activities of the foundation. The organization publishes its own journal, *Rubber,* which for the time being appears every two months. In addition "Communications" are periodically issued and distributed on a large scale not only in the Netherlands and Netherland India, but also in foreign countries, usually in French, German, and English, besides Dutch.

The 1937 program of the research department included problems connected with the combination of rubber powder with asphalt; latex and colloidal clay mixtures; investigation into the properties of latex and latex compounds; improvement of resistance to oil and heat; use of rubber for damping vibrations; uniting rubber to metal and concrete, etc. The work scheduled for 1938 covered, besides continued efforts to improve bitumen properties by the addition of rubber powder, the preparation and manufacture of rubber powder; the search for efficient methods of uniting rubber to other materials; investigation of the synthesis of rubber and the properties of synthetic rubber with a view to discovering possible pointers which might prove helpful in improving the qualities of plantation rubber. [From the *India Rubber World.*]

WHEELS OF FORTUNE. A SALUTE TO PIONEERS. Sir Arthur du Cros. Afterword by Arthur Roy du Cros. Chapman & Hall, Ltd., 11 Henrietta St., London, W. C. 2, England. Cloth, 5½ by 8½ inches, 316 pages. Illustrated. Index. Price 10s. 6d.

This book intimately reveals from behind the scenes the history of the invention of the pneumatic tire and the founding, 50 years ago, of one of the world's greatest industries. The author, one of the seven sons of the man who founded the original Dunlop Tyre Co., has written his book to honor the memory of Robert William Thomson, inventor of the pneumatic tire in 1845; John Boyd Dunlop, who in 1888 successfully applied the pneumatic principle to the wheels of cycles; Charles Kingston Welch and William Erskine Bartlett, who by their inventions of 1890 made pneumatic tires detachable and practicable for all forms of transport; and William Harvey du Cros, of Dublin, who allied invention with commerce and thereby founded the world-wide tire industry.

The story, which strikes a pleasing balance between the technical accuracy of legal and scientific history and the more intimate style of personal reminiscence, sheds much light on the early struggles of the pioneers of the tire industry. Full details of the invention and re-invention of the pneumatic are given, as well as subsequent developments, both legal and financial, which had a direct bearing on the commercial utilization of the tire. The book also brings in many interesting phases of the early days of steam coaches, hobby horses, bicycles and automobiles. The author pays tribute to, and recognizes the contributions of, many of the less generally known figures connected with the beginning of the tire industry. [From the *India Rubber World.*]

THE RUBBER INDEX, 1939. Part One, Chemicals, Compounding Ingredients, Etc. *The Rubber Age,* 88/89 Chancery Lane, London W. C. 2, England.

This 52-page directory refers to rubber chemicals available on the British market, and comprises an alphabetical list of manufacturers and suppliers, a group chart giving instant reference to manufacturers and suppliers of ten different groups of compounding ingredients, and six itemized charts giving references

to manufacturers and suppliers of chemicals in each of these ten groups. It contains also a list of chemical trade names. [From the *India Rubber World.*]

COMMODITY YEAR BOOK—1939. Compiled and published by Commodity Research Bureau, Inc., 82 Beaver St., New York, N. Y. Cloth, 8½ by 11 inches, 624 pages. Indexed. Price $7.50.

This book, which is to be published annually, is designed to fill a definite need for a comprehensive up-to-date reference on the many important commodities entering into commerce and industry. Other publications in the past have dealt with an individual commodity or group, but the present work is the first to include all of the leading commodities. The 1939 edition combines in one volume a statistical reference work, a raw material encyclopedia, and nine fact-finding studies on major commodity problems of a general nature. The book presents 120 chart illustrations in addition to the many tables, while relevant text material accompanies each set of statistics.

Thus, the section on rubber contains brief information on the history, uses and sources of rubber and a discussion of international production control. A 1938 chronology of important events affecting the rubber market is also presented. Rubber statistics, in the form of charts and tables, include data on prices, exports, stocks, absorption and basic quotas of agreement countries. Supplementary tables cover United States statistics on reclaimed rubber and production, shipments, and stocks of casings and tubes. [From the *India Rubber World.*]

INSIDE THE FLAME. By F. Burnham MacLeary. Godfrey L. Cabot, Inc., 77 Franklin St., Boston, Mass. 8½ x 11 in. 32 pp.

The story of the manufacture, properties and uses of carbon black, told in this booklet, was designed to supplement a sound motion picture produced under the title, "Inside the Flame," for Cabot by Caravel Films, Inc. The booklet, profusely illustrated with still photographs from the sound picture, skillfully traces the production of carbon black, compares its physical characteristics with other blacks, discusses its reactions with other materials, and stresses its importance in the manufacture of rubber products, quick-drying inks, lacquers, paints and plastics, and a variety of other finished products. Although written from a technical angle, the text is so worded that even the purely uninitiated will have a firm understanding of carbon black and its functions, after reading the booklet. [From *The Rubber Age* of New York.]

COLLOIDAL PHENOMENA. By Ernst A. Hauser. McGraw-Hill Book Co., Inc., 330 W. 42nd St., New York, N. Y. 1939. Cloth, 6 by 9 inches, 294 pages. Subject and name indexes. Appendix. Price $3.

The book, with sub-title "An Introduction to the Science of Colloids," is based on notes used as a text for the classes conducted by the author at the Massachusetts Institute of Technology. He states in his preface that it was not his intention to furnish another text book on colloidal chemistry, of which there are already a "sufficient number" in existence. What he set out to do was to acquaint the reader "in as simple a manner as possible with the modern viewpoints in colloidal science, and to show where and why they must differ from those so successfully applied to physico-chemistry." Having regard to the author's intentions and program, the incorporation of his personal opinion was necessary "to a greater extent than if he were merely to act as a chronologist in writing a formal textbook." In other words, Dr. Hauser has, broadly, given us his personal views on, or an attitude towards, a complicated and difficult subject, and has avoided anything in the nature of encyclopædic treatment.

The work runs to 272 pages, exclusive of indexes, etc., and is profusely illustrated, largely with diagrammatic sketches prepared by the author, with a view to explaining and simplifying the text. These sketches, I may add, are well conceived and executed. With a view to still further simplifying matters for the beginner, the essential mathematics of the subject appear in an appendix. The book is divided into 17 chapters, the headings to which afford a clue as to the general attitude of the author towards colloidal phenomena. They are roughly as follows: The Science of Colloids; The Disperse State of Matter; Terminology and Definitions; Difform Systems; Form and Shape of Matter; The Peculiarity of the Colloidal State; The Production of Colloidal Systems; Kinetics; Electrical Properties; Surface Phenomena; Protection and Sensitization; Dispersion; Coagulation and Dissolution; Particle Shape and Optics; Aggregates Bonded by Primary and Secondary Forces, respectively, and Colloidal Aggregates. Although the author suggests that this volume is mainly for the student or beginner, it should prove attractive and useful to a considerably wider range of readers, particularly in view of the subjective handling of the matter. [P. Schidrowitz in the *India Rubber Journal.*]

DICTIONARY OF SCIENTIFIC TERMS. (American Edition). Compiled by C. M. Beadnell. Chemical Publishing Co. of N. Y., Inc., 148 Lafayette St., New York City. 4¾ x 7 in. 235 pp. $3.00.

Although termed a "dictionary," this is actually a book of reference, based on notations taken from recently published scientific books and from articles in scientific periodicals. The author has selected those terms which are most likely to call for inquiry on the part of students and others, and in the case of many words has provided a fuller explanation than the somewhat terse one given in most dictionaries. A unique feature of the book lies in the numerous cross-references, synonyms and antonyms which enable users to quickly discover words of similar, related and opposite signification. [From *The Rubber Age* of New York.]

RUBBER TERMINOLOGY *

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INTRODUCTION

A definite part of scientific activity consists in applying words to connote materials and ideas. Observed phenomena and the hypotheses derived from them are systematized and generalized by means of such terminology. Progress itself depends on words or equivalent symbols, for we have no other means of exchanging information.

The universality of speech and writing tends to obscure the remarkable complexity of these processes, and the editor of *Chemical Abstracts*, in a recent admirable lecture[1], had occasion to deplore the numerous and serious deficiencies in chemical terminology.

All that he said of chemical words in general applies, with perhaps greater cogency, to the terminology of the rubber industry. The science and technology of rubber are but in their infancy. They have been superadded to an industry developed for a century by practical men in the rough-and-tumble of the works. It is not surprising, therefore, that verbal exactitude has scarcely been considered. The infant rubber science has, however, shown vigorous development in the last two or three decades, and there are signs that its attention is being awakened to the need for putting its verbal equipment in order.

The issue is not only a scientific one. It is complicated by commercial considerations which cannot be ignored. Pithy trade names are undeniably better sellers than cumbrous systematic chemical names. The persistent use by the leather and leather footwear industries of the term "substitute soleing," for what is, quite simply, rubber soleing, has undoubtedly prejudiced an excellent and serviceable product. The coining of some happy alternative, following the example of the replacement of "artificial silk" by "rayon," would probably have effects measurable in terms of dividends.

It must be realized, therefore, that any attempts to improve rubber terminology will be limited in some directions by trade considerations. That is not a reason why the industry's scientific literature, at least, should not be given all the clarity and precision that can be achieved. In the following discussion several directions are pointed out in which improvement would be welcome. The illustrative examples given are typical only and, unfortunately, are far from exhaustive.

SEVERAL TERMS WITH ONE CONNOTATION

It is perhaps a venial deficiency of rubber terminology that many of the industry's ideas have two, three or more names, since no standards exist to restrict such multiplication. Some authors seem to have a horror of using the same word twice, and the curse of the literary practice of "artistic variation" lies heavily on many rubber writings.

The basic word of the industry, rubber, has such variants in caoutchouc and, colloquially, gum. It is interesting to note that the two latter terms are duplicated

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 42, pages 1003-1009.

in French and German. The Deutsche Kautschuk Gesellschaft and the Verein Deutscher Chemiker have attempted to standardize their practice[2] by laying down the definitions: *Kautschuk*, raw rubber; *der Gummi*, vulcanized rubber; and *das Gummi*, gum (in general, as in gum arabic). Some authors[3] limit caoutchouc to the highly purified hydrocarbon, $(C_5H_8)_n$, as distinct from rubber in crude form, but the practice has no universality.

Hard rubber is perhaps more usually known by what was once a trade name, ebonite, and another former trade name, vulcanite, is not infrequently seen. References to white ebonite are especially incongruous.

Compounding ingredients in general figure under any of the terms fillers, drugs, chemicals, pigments or compounds. Examples of particular compounding ingredients with a variety of names are almost too common to call for mention[4]. A single illustration will suffice. The confusion in the carbon black group has been exhibited in painful detail by Scott[5]. The material often referred to as gas black, for example, has been named also carbon black, gas carbon black, carbon gas black, hydrocarbon black, hydrocarbon gas black, channel black, channel gas black, disc black, jet black, ebony black, satin-gloss black, silicate of carbon, and in a somewhat wider sense has been included in the names contact black, glossy carbon black, and smoke black. Surely this in itself demonstrates the case for standardization.

The product obtained when rubber and compounding ingredients are mixed together, ready for vulcanization, is known variously as a stock, mixing, mix, compound, blend or quality, and the practice of mixing or compounding may involve the use of a master-batch, mother-batch (or -stock), parent-stock, or base-stock (or -mix, or -compound). This plethora of names is by no means confined to the rubber works; every one of them can be found in serious scientific papers. There is quite a good selection in the papers of the present Conference.

The processes involved in obtaining stocks, or if preferred, mixings, receive equally generous treatment in regard to terminology. The rubber is masticated, broken down, plasticized, milled or softened. It may be extruded, tubed, spewed or forced. It is certainly vulcanized or cured. Thrown into emphasis in this way, this multiple terminology is not simply nescience but nonsense.

Such prodigality of terms arises, mushroom-fashion, overnight. Scientific infancy promotes the practice rather than serves as a check on it. Schidrowitz[6] recently pointed out the indiscriminate use of the terms coagulum, gel and jelly in the rubber industry's newest field, that of latex technology, and many other examples could be added.

ONE TERM WITH SEVERAL CONNOTATIONS

The terminology discussed in the preceding section may be absurd, burdensome to the memory, bewildering to the uninitiated, but it is not misleading. The use of a single term which has two or more meanings is a more serious defect of language. The intended meaning may often be determined by the context, it may sometimes be guessed on a basis of "customary practice," but sooner or later such terms are apt to involve the incautious reader in complete disaster.

The basic word of the industry, rubber, is an arch-offender. It can be used properly, as in the present Rubber Technology Conference. But it is used also, without qualification, to connote such diverse ideas as highly purified caoutchouc, raw or crude rubbers of many botanical types, soft vulcanized rubbers in endless variety, hard rubbers, synthetic rubbers and so-called synthetic rubbers. One

has but to think of such common phrases as the empirical formula of rubber, sheet rubber, rubber-soled shoes, oil-resisting rubber, to appreciate how much is taken for granted every day.

In a recent discussion[7] an engineer asked the question: what is the energy-absorbing capacity of rubber? Quite probably he would have been among those who smiled if a rubber technologist had asked: what is the hardness of metal? Yet rubber connotes quite as many substances of different properties as does metal. It would be a valuable service to users of soft vulcanized rubber, especially to engineers, if a series of definite types were defined and given definite names. Part of the original plan of "Rubber, Physical and Chemical Properties"[8] was to examine numerous samples of each of a series of commonly marketed "grades" of soft vulcanized rubber, adopt some suitable average or common quality as a standard type for each grade, prepare such standards, test them for a wide range of properties, and present the results *in extenso*. The grades provisionally selected were (with apologies for the only names available at the moment), "pure gum," U.K. Government specification T. G. 25 Quality C, tire tread, inner tube, cable insulation, soleing, "mechanical" quality containing magnesium carbonate, buffer (or spring), wringer roller, flooring, and hot-water bottle. It proved impracticable to carry out this project, but if and when it is done, the word rubber, at any rate in the domain of soft vulcanized rubber, will attain a precision at present very much lacking.

The term synthetic rubber has been the subject of much lively discussion in the last two years[9]. Broadly speaking, the controversy centres round the choice between two interpretations:

(*a*) that a synthetic rubber should be identical with, or at least closely related to, natural rubber in a chemical sense.

(*b*) that a synthetic rubber should reproduce the outstanding physical characteristics of natural rubber.

Synthetic rubber, under the first of these definitions, would probably be limited to polymers of butadiene and its homologs. Bruni goes so far as to admit also substituted butadienes, which brings Neoprene into the synthetic rubber category. The core of the argument is that synthetic rubber must have a particular hydro-carbon chain, some license being permitted as to the subsidiary chemical atoms or groups attached to the chain. The second definition boldly includes all materials that are "rubbery," a term which seems to be preferred to the more explicit "rubber-like." Under this generous cloak we may count as synthetic rubbers materials such as polyvinyl, polystyrol, and polyacrylic "resins," and even olefin polysulfides like Thiokol. There are only two ways of determining this dispute, by arbitrary standardization, or by natural selection and the survival of the more fit. It is useless to resort, for example, to the "New English Dictionary" (Oxford) for the meaning of the word synthetic. That work records what English practice is and not what it ought to be; in fact, while the interpretation (*a*) is the only one in agreement with the volume of 1919, the interpretation (*b*) has duly appeared in the 1933 supplement. It may be noted, however, that there is a tendency in the most recent rubber publications to say "synthetic rubber-like materials" rather than "synthetic rubber," while the Association Suisse pour les Essais de Matériaux[10] definitely includes polyvinyl and polystyrol compounds as resins, and not as synthetic rubbers, in a proposed international classification of moulded insulating materials.

Attempts have been made to cut the knot by proposing new names for the general group, such as "synthetic elastics." Alternatively, the name "synthetic

caoutchoucs" might be reserved for the butadiene group. Endeavors of this kind would probably end in a multiple terminology as objectionable and confusing as the present ambiguity.

The variety of meanings which affects the first word of the industry is in no way unique. Rubber is "cured" with smoke in a Malayan rubber factory, and by vulcanization in a British rubber factory. No one could say off-hand what has been done to a sample of rubber if all that he knew was that it is "vulcanized"—the term includes a dozen processes. Soft vulcanized rubber "ages," naturally on the shelf, or in sunlight; artificially in oven or bomb or under an ultra-violet lamp; in service on a car wheel or in a petrol pump. All these occurrences have been described in scientific papers as "aging," without qualification.

The rubber industry is scarcely to be blamed because a "tire cover" may be the tire casing on the wheel or the box at the rear of the car, nor for the irritating ambiguity of the word "hose," these are faults in the English language. It must, however, use all such terms with an adequate realization that they have two or more meanings.

TERMS WITH FALSE CONNOTATIONS

The terms to be discussed in this section are not necessarily troublesome to the rubber industry itself, but they may be very troublesome to those outside. For they are terms with precise connotations in their own spheres and different connotations when applied to rubber.

Outstanding examples are the words used to describe the elastic properties of soft vulcanized rubber. Mathematicians and engineers have evolved a set of precisely defined terms for the elastic properties of metals and other rigid materials. These terms, however, are either not exactly applicable to rubber or are definitely misleading when so applied. In spite of this, rubber technologists make free use of the common engineering terms without any special qualifications. Rubber men, or at any rate some of them, appreciate the altered connotations, but the outsider must frequently be eluded. The term "modulus" will come to the mind at once. The majority of rubber technologists now use this word. Some give it a definite connotation, to signify a stress at a predetermined extension. Others use the word in a rough-and-ready qualitative sense; a "high-modulus" rubber, for example, may often mean nothing more than a stiff, tough, or even hard rubber. No engineer would dream of using the word in either sense, for it is a purely mathematical term which properly connotes a coefficient in an equation.

The large extension to which soft vulcanized rubber may be submitted, the consequent large change in cross-sectional area of the extended material, and the markedly curvilinear form of the stress-strain curve, render the ordinary theory of elasticity of rigid materials inapplicable. Terms such as "modulus of direct elasticity" or "Young's modulus," and "modulus of transverse elasticity or shear," are correctly used only when infinitesimal strains are in question. In the face of the large finite strains that occur in rubber they are not only meaningless but false. Rubber has neither a yield point nor an elastic limit in any real engineering sense. Yet all these terms may be found in rubber literature.

Perhaps the most unhappy term in this group is "rigidity." Rubber technologists have used this word to convey the idea now generally expressed by them in the word modulus, implying resistance to extension. The engineer uses it exclusively to indicate resistance to shearing.

It should be noted, also, that the engineer uses all the foregoing terms to denote *constants* of his materials, definite numbers which characterize the materials and

their behavior. None of the properties involved is constant for soft vulcanized rubber, but depends on the magnitude of the applied strain, the elastic history of the specimen and its age.

It is much to be hoped that some of these terms can be rescued from their present distortion in the rubber industry, but one of them, "modulus," is irretrievably corrupted.

False use of a word may result in costly consequences. Quite recently a confusion between the processes of skim-coating and friction-calendering, and the misapplication of the word calendering to connote the latter, caused the loss of a patent suit[11]. The writer, in the first text of "Rubber, Physical and Chemical Properties," used the word magnesia in good faith that its meaning of magnesium oxide would be understood. There was a prolonged overhauling of the proofs when several experienced rubber works' chemists agreed that no rubber compounder would think it meant anything but magnesium carbonate.

TERMS WITH NO EXACT CONNOTATION; JARGON

The use of meaningless words is not peculiar to rubber science, nor to science in general; it is a fault of all men. But the magnitude of the fault is relative, depending on the knowledge of the reader or listener. What may be unintelligible jargon to one man may be an elegant expression of beautiful ideas to another.

Yet the most intelligent find it necessary to resort to jargon at some advanced stage of their work. Materials, processes, hypotheses have to be given names long before we properly understand their full implications. Such provisional names may be used for long periods of time as if they stood for understandable things. But understanding grows, and the jargon of yesterday may gain definiteness tomorrow. At the same time constant vigilance is necessary, lest these dangerous symbols of assumed knowledge become so familiar as to be accepted as honest terms.

One has but to think of the light that has been thrown on our knowledge of such terms as depolymerize and vulcanization (in reference to normal sulfur vulcanization) to appreciate that these words are well on their way to becoming real.

There are many analogous terms awaiting explanation and interpretation. Hardness, for example, is a simple word in daily use in the laboratory of any rubber works. But, as pointed out by Lunn[12], when we consider the way in which we measure this property, the absence of anything approaching fundamentality in the term is depressing. An arbitrary indenting tool, an arbitrary load, an arbitrary time period, an arbitrary scale of readings—we may well ask, what is hardness? Nevertheless, if hardness, like many similar terms, is for the moment pure jargon, it is legitimate jargon, for there is hope that one day its meaning will be elucidated.

Unfortunately, besides the working jargon of the moment, which is slowly being transformed into serviceable terminology, we have with us far too many terms which are never likely to mean anything.

The swarm of trade names, for example, with which the rubber industry is beset is lamentable. Crane[1] has said of them: "trade names—of these there is no end. They multiply and they linger. If they are an evil they are no doubt a necessary evil. I do not gainsay their usefulness in trade. They are, however, the bugbear of scientific record-keepers. Frequently they get into technical literature without definition or analysis. . . . Technical literature is not fiction, I mean it should not be. If Edna Ferber, in a story, wishes to name a mysterious character 'Esmeralda' it is all right. Without an unmasked picture of the heroine

Esmeralda's activity in a paper by John Scientist on the preservation of rubber is much less exciting."

His remarks are scarcely strong enough. The "secrecy complex" in a scientific paper may render it not merely unexciting but so much waste paper.

If trade names have the excuse of financial interest, what can be said in favor of such terms as "pure gum stock," "tread stock," or "mechanical rubber goods" colloquially known as "mechanicals." The variety of ingredients that may figure in "pure gum" is astonishing. "Tread stock" is a handy sliding term that means almost any kind of tough strong rubber in which the writer chances to be interested; it might mean a little more if dated, tread stock 1921, tread stock 1938, for example. "Mechanicals" are legion, but no two rubber technologists could agree as to all the goods included in the term. Such slipshod terms as these mean nothing by themselves. They should never be used except as short terms for previously defined conceptions.

STANDARDIZATION

It is evident that any standardization of rubber terminology, however slight, will be all clear gain. No steps towards improvement can be made, even by the most willing author, until the industry is provided with an agreed glossary.

There are various unofficial glossaries already in existence, of which the following may be noted:

H. C. Pearson, "Glossary of Words and Terms used in the Rubber Industry"[13].

R. T. Vanderbilt Co., "Glossary of Terms used in Rubber Technology"[14].

T. R. Dawson and B. D. Porritt, "Glossary"[15].

Stamford Rubber Supply Co., "Glossary of Terms for Rubber Manufacturers"[16].

Dunlop Research Laboratories, "Glossary"[17].

The first of these in parts is encyclopedic in character, considerably exceeding the limits of formal definition of terms. None of them has been written from the point of view of standardization, simplification and systematization. Something much more authoritative is necessary.

It is of much interest and importance to note that the Rubber Products Committee D-11 of the American Society for Testing Materials has in its program of current work[18] the preparation of a glossary for rubber, with a view to putting on record terms that will be recognized as standard. However, it ought to be realized that the work is essentially one for international effort. It is earnestly to be desired that the British Standards Institution should establish a similar program, and carry it out in the closest collaboration with the A.S.T.M. Nothing short of complete agreement between the American and British Committees, except perhaps in the matter of spelling, will be really satisfactory. The American and British Library Associations, in joint committee, succeeded in agreeing to the last comma on cataloging rules despite the endless intricacies of the work, and there is no reason why American and British rubber men, also in joint committee, should not have equal success in a standard glossary.

Eventually, the work should be given still wider international scope, aiming at agreement on the equivalent Dutch, French, German and Italian terms. It is worth consideration, also, that the subject is one which affects more than the rubber industry. Parts of rubber terminology are common to paint terminology and plastics terminology, for example. In this connection it is of interest to note[19] that Committee ISA-35 of the International Federation of National Standardizing Associations, which held a first session in 1936 in Budapest at the International Standardization Congress. appointed a sub-committee to standardize the vocabu-

lary of the pigment, paint, and varnish industry, in three languages. The work of this sub-committee is clearly of direct importance in any standardization of rubber terminology.

It must not be anticipated, however, that a standard glossary will immediately revolutionize the verbal deficiencies of every rubber writer. There is a proverb about a horse and water. But with an agreed glossary in being, at least every teacher and author of good will can add his quota to improve the situation.

The author wishes to thank the Board of Management of the Research Association of British Rubber Manufacturers for permission to publish this paper.

REFERENCES

[1] *Chem. & Ind.* **56**, 1105 (1937).
[2] *A. T. Z.* **36**, 541 (1933). See also *Gummi-Ztg.* **45**, 540 (1930); **47**, 785 (1933); *Tech. Handel* **23**, 139 (1933).
[3] Porritt, "Chemistry of Rubber", London, **1913**, p. 1.
[4] See, for example, Rabaté, *Intern. Assoc. Testing Materials*, London Congress, **1937**, p. 514, on the terminology of the pigment, paint and varnish industry.
[5] *J. Res. Assoc. Brit. Rubber Manufrs.* **4**, 11 (1935).
[6] Communication, **1938**.
[7] *Bull. Rubber Growers' Assoc.* **19**, 568 (1937).
[8] Dawson and Porritt, "Rubber: Physical and Chemical Properties", Croydon, **1935**.
[9] Stevens, *Chem. & Ind.* **55**, 276, 328, 443, 814 (1936); Naunton, *Chem. & Ind.* **55**, 297, 328 (1936); Barron, *Chem. & Ind.* **55**, 843 (1936); Schidrowitz, *India-Rubber J.* **92**, 177 (1936); Cholet, *Rubber Age*, (N. Y.) **41**, 256 (1937); Stillwagon, *India Rubber World* **97**, No. 3, 54 (1937); Fleurent and Bruni, "Recueil des Communications", Congrès Internationale du Caoutchouc, Paris, **1937**, pp. 177, 182.
[10] *Rev. gén. mat. plastiques* **13**, 138 (1937).
[11] "Reports of Patent, Design and Trade Mark Cases", **54**, 151 (1937).
[12] *Vanderbilt Rubber Hand Book*, **1927**, p. 7.
[13] *India Rubber World* **63**, 235, 325, 404 (1920-21); **64**, 481, 561, 723, 882 (1921); **65**, 7, 93, 171, 263, 412 (1921-22); **66**, 483, 540, 605, 671, 739 (1922); **74**, 65, 127, 189, 251, 313 (1926).
[14] *Vanderbilt News* **2**, No. 1, 4 (1932).
[15] "Rubber: Physical and Chemical Properties", Croydon, **1935**, p. 599.
[16] Stamford, Conn., **1935**, p. 27.
[17] *Dunlop Gazette* **16**, No. 12, 8 (1936); **17**, No. 3, 6; No. 5, 2 (1937).
[18] "A.S.T.M. Bulletin", No. **90**, 37 (1938).
[19] *Intern. Assoc. Testing Materials*, London Congress, **1937**, p. 517.

THE COMPOSITION AND CHARACTERISTICS OF THE RUBBER IN HEVEA LATEX*

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IMPORTANCE OF THE SERUM SUBSTANCES

The importance of the non-rubber components of latex, and particularly the protein components, in deciding the behavior towards coagulating agents was recognized at a relatively early date[1]. Indeed, some investigators regarded the coagulating effect as being exerted only by way of the protein, the addition of the coagulants leading initially to its precipitation from solution in the serum, and thereby to the aggregation of the rubber globules.

To-day the stability of latex as an aqueous dispersion of rubber globules is still regarded as being dependent on the non-rubber components of the latex. The material actually responsible for its stability, however, is now known to be adsorbed on the surface of the globules, and the physical behavior of the latex globules towards extraneous influences depends on the adsorbed film rather than on the rubber. This is remarkable, as the adsorbed layer, based on the approximation[2] that one gram of protein covers a surface area of 10^7 cm.^{2}, probably constitutes only 0.6% of the weight of the rubber globules, or thereabouts. The protective layer is not immovably attached, although in fresh latex it is possibly more firmly held than in preserved latex[3]. It should be noted that the adsorbed coating normally represents only a small fraction of the total hydrophilic surface-active substances in the latex, and the stability of latex is less influenced by decrease in the proportion of the non-rubber components than might at first be expected. Latex purified by triply centrifuging shows little, if any, increased tendency to coagulation.

NATURE OF THE ADSORBED LAYER

In normal circumstances with fresh or preserved *Hevea* latex the exposed surface of the protective layer is doubtless of protein character, and the physical behavior of the rubber globule can be simulated by a "synthetic" particle, in which a nucleus of hydrophobic material, not necessarily rubber, is surrounded by an adsorbed protein film. Special conditions may arise, however, in preserved and compounded latex leading to removal of part of the protective protein film and even to partial or complete replacement by a film of other composition. At certain degrees of dilution and *p*H of the serum, the protein of ordinary ammonia-preserved latex may, for instance, become partly replaced by natural fatty acid. Indeed, by comparison of the electrophoretic behavior of artificial dispersions of particles both unprotected and having protective coatings of natural protein and natural fatty acid, respectively, with the behavior of preserved latex, it has been shown that on dilution a gradual disappearance of part of the protein sheath is accompanied by a partial formation of a protective layer of fatty acid[4].

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These experiments and deductions are possible on the assumption that the electrophoretic behavior of the dispersed particles depends quantitatively on the nature of the surface presented to the aqueous phase. It would have been surprising if the protein in latex had proved to be a single chemical substance, and investigation[5] has revealed the existence of at least two insoluble protein substances in the serum, with isoelectric points at *p*H 4.55 and 3.9, respectively. The electrophoretic behavior of the rubber globules in the latex indicates that the adsorbed film is normally provided by the former of these.

The behavior of fresh and ammonia-preserved latex, and also of artificial dispersions in which the dispersed particles are covered by protective layers of the protein components of the serum, provides evidence that the external surface of the globules has similar chemical nature in all three cases. However, the protective layer is not necessarily of uniform composition throughout its depth. It is probably orientated with respect to the rubber-water interface. Furthermore, some authorities believe that the protein on the rubber globules is actually present in the form of a "protein-lipin" complex[6]. As electrophoretic examination throws light only on the nature of the surface presented to the aqueous phase, the stated experimental demonstration of the protein character of the protective coating would be quite consistent with this possibility and would indicate that the molecules of any such complex are orientated with their protein characteristics exposed externally. The evidence for the "protein-lipin" complex is slender, but its postulated existence can be made to afford a tentative explanation of certain distinctions between fresh and preserved latex. When brought to the isoelectric point of the protein, fresh latex undergoes a slow thickening until, after hours, it forms a uniform reticular mass of coagulum. In contrast, the uniform acid-coagulation of ammonia-preserved latex is difficult, the addition of the acid resulting in immediate local coagulation which tends to prevent uniform distribution. The slow coagulation rate and the formation of a uniform, reticular mass of coagulum with fresh latex may be associated with an orientated adsorbed layer of the protein-lipin complex. In ammonia-preserved latex, on the other hand, the presence of the alkali may have resulted in the fission of the "protein-lipin" complex[7], the lipin products passing into the serum and the protective layer becoming entirely protein in character. This hypothesis may provide also an explanation for the observation that, whereas the adsorbed interfacial layer on the globules in fresh latex is not readily desorbed[3], the protein adsorption in ammonia-preserved latex is readily reversible[4].

HYDRATION OF THE RUBBER GLOBULE

The fact that the protein film in the presence of water is naturally in a state of hydration appears to have led to exaggerated ideas as to the degree of hydration of the rubber globules in latex. Both in the technical literature[8] and in patents[9] extensive hydration has been postulated or inferred[10]. The reduction in the viscosity of latex with rise in temperature is of normal magnitude however, and gives no indication of any extraordinary decrease such as would be expected if considerable dehydration of the rubber globules accompanied the temperature change. Furthermore, although the dissolved protein in the serum of latex undergoes partial precipitation or denaturation at 80° to 100° C., the isoelectric *p*H of latex (which is actually that of the adsorbed protein film) is not appreciably altered by heating at 80° C. for several hours. For the experimental results of Table I, indicating the permanence of the substantially unchanged protein film throughout such treatment, we are indebted to I. Kemp.

DEPROTEINIZED RUBBER

From the point of view of the various latex processes for manufacturing rubber goods the protective protein layer is desirable. Indeed, it is the practice, as is well known, to introduce additional stabilizing agents, and some of these doubtless enter to some extent into the protective layer around the globules. This is evident from the fact that with the addition of certain of such artificial stabilizing agents the isoelectric *p*H of the latex undergoes considerable alteration[11].

In the production of massive rubber from latex a considerable proportion of the material dissolved in the serum, as well as that adsorbed on the globules, persists in the dried rubber. For some purposes, however, rubber is required as free as possible from protein and other non-rubber substances. While the "deproteinization" of rubber by heating rubber (or latex) with superheated water or with alkaline solutions effectively removes protein, the treatment is not without influence on the rubber itself. The alternative procedure by repeated creaming or centrifugal separation of latex at ordinary temperatures has the advantage of removal of the free serum solids and a proportion of the adsorbed protein without impairing the mechanical qualities of the dispersed rubber.

TABLE I

EFFECT OF HEATING ON THE ISOELECTRIC *p*H OF AMMONIA-PRESERVED PLANTATION LATEX

Dilution	Isoelectric *p*H of unheated latex †	Heat treatment	Isoelectric *p*H of latex after heating †
1: 25,000	3.7–3.8	10 mins. at 80–85° C.	3.7–3.8
		20 " "	3.8–3.9
		60 " "	3.8–3.9
		60 " " *	3.8–3.9
		330 " at 80–100° C.*	3.7–3.8
1: 400	3.7–3.8	330 " " *	3.9–4.0
1: 200	4.0–4.2	330 " " *	4.0–4.2
Undiluted (35% rubber)	4.4–4.5	—	—

* Latex heat-treated after dilution with equal volume of water; further dilution to stated degree after heat treatment.
† In acetate buffer of "ionic strength" 0.01.

The reduction in the concentration of serum solids by repeated dilution and centrifugation naturally tends to decrease the amount of protein adsorbed on the globules. In some cases the globule surface becomes partly uncovered. We are indebted to I. Kemp for the following experimental results.

First, in a triple centrifuging process in which the 60% cream obtained from ordinary 35% latex is rediluted with water and is again submitted to successive processes of centrifuging, dilution and centrifuging, the concentration of serum solids in the aqueous phase of the final 60% cream (disregarding for simplification the small amount liberated from the surface of the globules) will be approximately 0.148 that of the original. Reference to the curves for the relation between the dilution of (the aqueous phase of) normal latex and the proportion of the globule surface covered by protein[12] shows that the fraction of the globule surface covered by protein is 0.84. If the triply centrifuged cream is finally rediluted to the original 35% concentration, the new concentration of serum solids in the aqueous phase corresponds with a protein covering over 0.6 of the globule surface.

Secondly, the relation of the isoelectric *p*H of the latex to the extent of protein covering of the globule is known[13]. Measurement of the coagulation *p*H affords

a convenient method for determination of the approximate isoelectric point; the following figures are the averaged results of electrometric experiments at 20° C:

	Dilution at coagulation (original concentration=1)	Mean *p*H for coagulation	Approx. fraction of globule surface covered by protein
Normal 60% latex.....	0.132	4.0	0.8
(*i.e.*, once centrifuged)	0.270	4.6	1.0
Triply centrifuged	0.147	2.7	0.2
60% latex	0.295	3.3	0.5

Having regard to the differences in rubber content, these figures are in reasonably good accordance with the other figures above.

CREAMING OF LATEX

Although "cream" can be observed on the surface of ammonia-preserved plantation latex after long standing[14], the natural tendency in this direction is slight because the buoyancy forces are insufficient to superimpose any considerable upward drift on the irregular Brownian movement of the individual globules. Spontaneous creaming is accompanied by the formation of reversible agglomerates of rubber globules. Means which have been adopted to increase the spontaneous creaming effect, *e.g.*, excessive dilution (500 times) with aqueous solutions of non-coagulating electrolytes[15], or dilution with 5% sodium hydroxide solution[16], do so by enhancing the natural clumping effect. Dilution decreases the concentration of the hydrophilic substances in the bulk of the aqueous phase and so decreases their degree of adsorption[4]; the presence of electrolytes, by ion adsorption, reduces the electric charge on the globules. The addition of caustic soda, by bringing about rapid degradation of the proteins and increasing their solubility, causes their partial removal from adsorption on the globules. All these methods enable the globules more readily to approach and cohere, and the enhanced clumping is not directly due to reduction in the Brownian movement. Cream formation by the controlled reduction of *p*H[17] is probably the result of irreversible microcoagulation. On the other hand the tendency of latices of high rubber content to become more concentrated in their upper layers can be attributed, at least in part, to restriction of the Brownian movement of the globules owing to the closeness of their packing.

ORGANIC CREAMING AGENTS

The spontaneous creaming of milk is due to a reversible agglomeration of the protein-protected fat globules; it can be assisted by dilution, and still more by the addition of low proportions of gelatinous or mucilaginous substances such as gelatin, Irish moss, Iceland moss and agar. Analogously these creaming agents were applied to latex[18]. It is found that by using suitable proportions, latex in 24 hours will give a quantitative yield of a cream containing 55 to 60% rubber.

With a few notable exceptions such as gelatin and polyvinyl alcohol, nearly all creaming agents belong to the ill-defined class of compounds designated "gums." They have no pronounced characteristics in common, apart from their high molecular weight, their hydrophilic nature, and the high and anomalous viscosity of their aqueous solutions; most of them form jellies with water. It seems probable that their creaming power is associated with their common feature of closely spaced polar groupings such as $-OMe$, $-OH$ and $-COOH$, which enable

their molecules to associate by semi-polar linkings or by local dipole attractions to form ramifying aggregates (see later). An account of creaming agents from a chemical point of view has been given by Baker[19]. From time to time many new substances have appeared in the patent literature as creaming agents[20], but their disclosure has not aided elucidation of the creaming action.

CLUSTERING OF GLOBULES IN CREAMING

These substances bring about a marked thickening in latex, and the rubber globules form reversible clusters visible to the naked eye. The clustering process has been followed with the aid of the microscope. On the addition of the creaming agent, the Brownian movement is considerably reduced and the particles form groups in a manner indistinguishable from flocculation. The groups are, however, disaggregated by movement of the cover-glass and fresh clusters form on standing (cf. Baker[19]).

When ammonia-preserved 30% latex containing sufficient creaming agent is allowed to stand, a slowly increasing volume of serum or "skim," containing little or no rubber, separates at the bottom of the containing vessel. The plane of separation of cream and skim moves slowly upwards, the cream throughout containing all, or nearly all, the rubber. In the creaming of milk, by contrast, a gradually increasing volume of cream collects at the upper surface and the cream-skim division plane moves downwards. With lower proportions of creaming agent, the rubber is not completely retained in the cream layer, and the skims contain appreciable quantities of rubber.

MINIMUM AND "OPTIMUM" PROPORTIONS OF CREAMING AGENT

Experiments directed to the purpose showed that the minimum proportion of creaming agent (calculated on the aqueous phase) to give a rubber-free skim is substantially constant for any one creaming agent and independent of the rubber content (10 to 48% rubber). Furthermore, the proportion is independent of ammonia content (0 to 2%), and of *p*H (7.3 to 11.5). With one exception all the creaming agents investigated show a very slight but definite decrease in efficiency with increase in serum solids content (0.2-2.4% on aqueous phase). The efficiency of methyl cellulose increases with increase in serum solids content within the above limits. Replacement of nearly all of the serum solids by roughly equivalent proportions of other surface-active substances, *e.g.*, peptone, sulfonated castor oil, soaps, saponin or casein (by adding these to triply centrifuged latex containing about 0.1% of serum solids) is without effect on the efficiency of any of the creaming agents. The presence of a high proportion of casein, however, appreciably reduces the efficiency of all the creaming agents.

The minimum proportion of creaming agent capable of converting all the rubber to cream is here termed the "optimum" proportion. Table II shows the optimum proportions of some creaming agents determined by experiment.

TABLE II

Creaming agent	Optimum proportion (% calculated on the aqueous phase)
Irish moss	0.091
Gum tragacanth	0.107
Methyl cellulose (Tylose S100)	0.292
Sodium alginate	0.211
Locust bean gum	0.135

Using optimum proportions of various creaming agents in latices with a serum-solids content of 1.0% on the aqueous phase, all the creams after a period of 4 days have approximately the same rubber content, 67% by weight, irrespective of the original rubber content. With increase in the serum-solids content, the creams (after 2 days) are of somewhat higher rubber content. Estimation of the rubber content of the skims from latices containing proportions of creaming agents below the optima showed that the amount of rubber carried up (and consequently also that left in the skim) is influenced by the amount of creaming agent employed, but is not directly proportional to it. Figure 1 gives results with methyl cellulose (Tylose S100) and sodium alginate.

Incidentally the rubber content of the skim is found to be independent of the shape of the containing vessel, and to be constant at all stages of its separation.

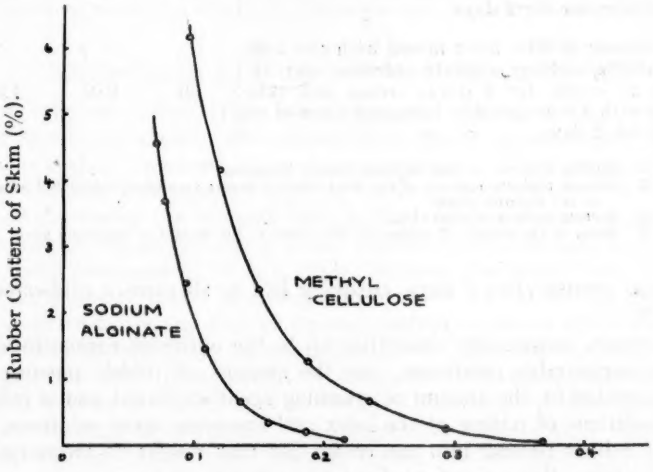

FIG. 1.

Skim separated from the cream shows no further tendency to cream, but creams may continue to exude skim even after several days. With extremely low creaming agent proportions, insufficient to cause visible creaming, the occurrence of creaming can be demonstrated by an analysis of samples from the top and the bottom of the columns. In a vertical column of 30% latex, 70 cm. long and 2.5 cm. in diameter, containing 0.025% of Irish moss (calculated on the aqueous phase), 5 cc. drawn from the bottom after 50 hours showed 21.9% rubber, and a similar sample drawn 3 cm. below the upper surface showed 42.3%.

REVERSIBILITY OF "CLUSTERING"

The reversibility of the association of the rubber globules induced by creaming agents is illustrated by the following typical experiments in which latex was treated with sodium alginate under different conditions. Similar results were obtained with other creaming agents (methyl cellulose and Irish moss).

	W	X	Y	Z
A. One volume of 60% (centrifuged) latex mixed with one volume of 0.31% sodium alginate solution and allowed to cream for 2 days.	30	0.22	Nil	193
B. One volume of 60% latex mixed with one volume of 0.31% sodium alginate solution and allowed to cream for 2 days; cream and skim mixed with 2 volumes of water and again allowed to cream for 2 days.	15	0.09	Equal, approx. 2%	174
C. One volume of 60% latex diluted with two volumes of water, allowed to stand for one hour, mixed with one volume 0.31% sodium alginate solution and allowed to cream for 2 days.	15	0.09		
D. One volume of 60% latex mixed with one volume of 0.10% sodium alginate solution and allowed to cream for 2 days.	30	0.07	4.1	559
E. One volume of 60% latex mixed with one volume 0.29% sodium alginate solution and allowed to cream for 2 days; cream and skim mixed with 4 volumes 30% latex and allowed to cream for 2 days.	30	0.07	4.3	557

Column W Rubber content of final mixture before creaming.
X Sodium alginate content of the final mixture before creaming, calculated as a percentage of the aqueous phase.
Y Rubber content of final skin.
Z Ratio of the weight of rubber in the cream to the weight of creaming agent used.

The final creams after 2 days' creaming had in all cases a rubber content of about 60%.

These results incidentally show that up to the optimum concentration, under otherwise comparable conditions, (*a*) the amount of rubber passing into the cream is decided by the amount of creaming agent employed and is independent of the conditions of mixing of the latex and creaming agent solutions; (*b*) the weight of rubber passing into the cream per unit weight of creaming agent is greater the lower the proportion of creaming agent.

ADSORPTION OF THE CREAMING AGENT

Using latex containing 30% of rubber and normal proportions of creaming agents (not greater than about 1.5 times the optimum proportion) it can be shown that the concentration of the creaming agent in the aqueous phase of the resulting skim is about one-half of that calculated for the aqueous phase of the original mixture. The proportion of creaming agent in the skim was estimated in two ways: (1) by a comparison of the viscosity, after making allowances for content of rubber and serum solids, with the viscosity-concentration relationship of aqueous solutions of the creaming agents containing the same proportion of ammonia, and (2) by creaming power in a fresh quantity of latex, the rubber content of the secondary skims being compared with a previously determined set of results for the relation between the rubber content of skim and the proportion of creaming agent. With creaming agent proportions higher than about 1.5 times the optimum the creaming-agent contents of the skims are greater than one-half of those in the original aqueous phases. Table III records experimental results obtained using sodium alginate as the creaming agent, with latex containing 30% of rubber.

TABLE III

(a) Sodium alginate % on aqueous phase in original latex	(b) Sodium alginate % in the skim (viscosity method)	(c) Ratio b : a	(d) Sodium alginate % in the skim (creaming power method)	(e) Ratio d : a
0.372	0.25	0.66	0.24	0.65
0.314	0.79	0.60	0.19	0.61
0.257	0.16	0.60	0.15	0.58
0.200	0.11	0.57	0.11	0.55
0.229	0.128	0.56	0.13	0.57
0.143	0.075	0.52	0.075	0.52
0.129	0.067	0.52	0.065	0.50
0.114	0.061	0.54	0.06	0.53
0.100	0.057	0.57	0.055	0.55
0.0858	0.050	0.58	0.045	0.53
0.0715	0.045 *	0.63 *	0.035	0.49
0.0572	0.042 *	0.74 *	0.03	0.53

* These figures are subject to a considerable experimental error owing to the high rubber contents of the skims.

EXCEPTIONAL FEATURES OF METHYL CELLULOSE

Methyl cellulose differs from other creaming agents in that, while most creaming agents are slightly less efficient with higher serum-solids contents, its efficiency is slightly increased in these circumstances. This anomalous behavior of methyl cellulose is demonstrated by the following experiments. Stable aqueous paraffin-oil dispersions can be made, using methyl cellulose as the stabilizing agent, but these dispersions do not cream in the present sense, although, owing to their comparatively large size (2 to 4μ), the oil droplets rise slowly and individually through the aqueous phase; creaming can, however, be induced by the addition of surface-active materials, such as saponin, sulfonated castor oil, or latex serum solids, which normally have no creaming effect. This was not observed with creaming agents other than methyl cellulose. Methyl cellulose consequently is exceptional because the presence of an auxiliary surface-active substance is necessary to its creaming effectiveness. This observation appears to be related to the fact that, whereas the normal creaming agents can satisfactorily cream latex repeatedly for an indefinite number of times (the skim being removed and the cream diluted and treated with a fresh solution of the creaming agent), methyl cellulose can only be used for repeated creamings if an auxiliary surface-active substance is introduced at each skim replacement. A similar observation has been reported in connection with the accelerated sedimentation of coal washing slurries by hydrophilic substances[21]. Some slurries which are difficult to flocculate by the hydrophilic substances alone are readily flocculated by their aid in the presence of an auxiliary surface-active substance.

RATE OF CREAMING

The proportion of creaming agent influences not only the quantity of rubber transferred to the cream, but also the rate at which the skim separates. Above the optimum proportion (see above) the rate of separation of skim falls off rapidly and at a greater rate than would be anticipated merely from the increase in the viscosity of the serum. Below the optimum proportion the rate is practically unchanged until roughly a proportion of one-half of the optimum is reached, below which the rate again decreases. Thus, at the optimum proportion, completeness and rapidity of separation are combined. Further, separation of skim

does not commence immediately in the latex-creaming agent mixture, but is almost invariably preceded by an induction period. This may be of several hours' duration, and is longer the greater the proportion of creaming agent. Vigorous agitation during or after the addition of the creaming agent solution somewhat reduces the induction period[22].

These observations are based upon series of experiments with latex of both 20% and 30% rubber contents, using several creaming agents, in which the movement of the plane of separation of cream and skim was followed, using latex columns 70 cm. long in glass tubes 2.5 cm. diam. Typical results for 30% latex at 21° ±2° C. are shown in Figures 2 and 3, and the appearance, after 48 hours, of the tubes of experiments 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19, using sodium alginate as the creaming agent, is shown in Figure 4.

In a comparson of creaming agents it is essential to use them at their respective optimum concentrations, or at concentrations which are equal multiples or fractions of these; such concentrations we term "equivalent" concentrations. In such a comparison, it must be emphasized that while, under standardized conditions, the production of skims of definite rubber-content is reproducible with a fair degree of accuracy, the progress of creaming, even using identical mixtures, may vary considerably, and for trustworthy results it is necessary to consider the average of many experiments or the general trend of a series of experiments.

FURTHER CONSIDERATION OF THE MECHANICS OF CREAMING

From observations during these experiments and from examination of the curves showing the relation of skim-volume to time, creaming is found to take place in three distinct ways, depending on the manner of aggregation of the rubber globules; the chief factor in this is the proportion of creaming agent, the contents of rubber and serum solids being subsidiary. With very low proportions of creaming agent a fraction of the rubber globules aggregates into small, isolated clusters which migrate independently and more or less according to Stokes' law, eventually collecting at the upper surface where, with the exudation of enmeshed serum, they may become a uniform layer. The remainder are apparently unaffected. With high proportions of creaming agent all the rubber globules aggregate into large, loose flocks leaving some free serum. The flocks first rearrange themselves with the exudation of the free serum and then slowly become more compact by the exudation of the entrapped serum. With intermediate creaming-agent proportions, the globules tend to arrange themselves in loosely interlocking groups in a substantially continuous three-dimensional network or reticular structure which exudes serum. The force tending to bring the flocks or groups together and expel serum is derived from the buoyancy of the individuals and not from any mutual effect. The optimum proportion of creaming agent (as defined above) is not the minimum for the formation of a complete loose structural association of the globules; the described shrinkage of the loose reticular aggregation and the migration of clusters can occur concurrently over an appreciable range of concentration of creaming agent. The double inflection in the earlier portion of the creaming curves (Figs. 2 and 3), especially for proportions of creaming agent near the optimum, shows the gradual alteration in the creaming process from substantially one of cluster migration to one of network shrinkage.

Similar types of separation have been observed in the sedimentation of clay suspensions rendered thixotropic by the addition of electrolytes[23] and of other disperse systems, *e.g.*, aqueous dispersions of quartz particles, rendered thixotropic by the addition of minute proportions of gel-forming materials, *e.g.*, alumina[24].

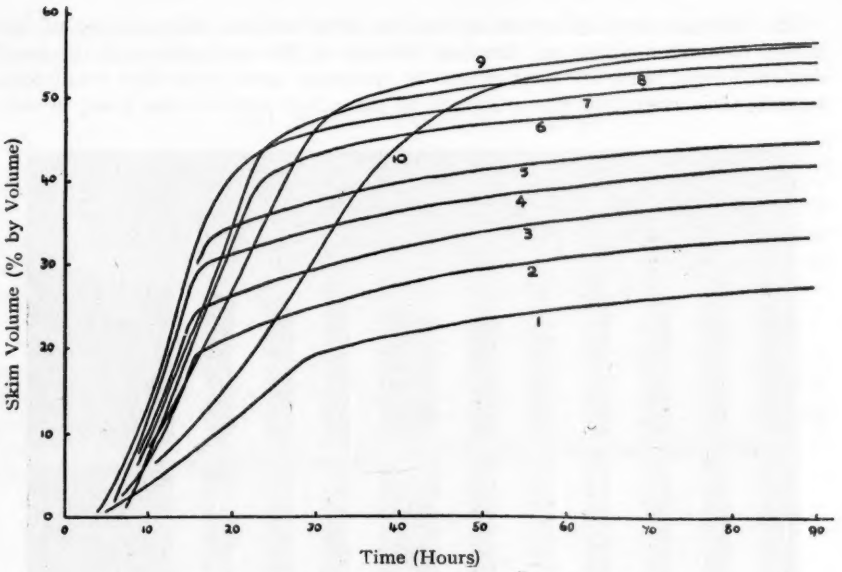

FIG. 2.—Creaming of 30% latex using methyl cellulose.

Curve	1	2	3	4	5	6	7	8	9	10
Methylcellulose on aqueous phase	0.715	0.572	0.458	0.366	0.293	0.234	0.187	0.150	0.120	0.096%

Skim contained some rubber (see Fig 1).

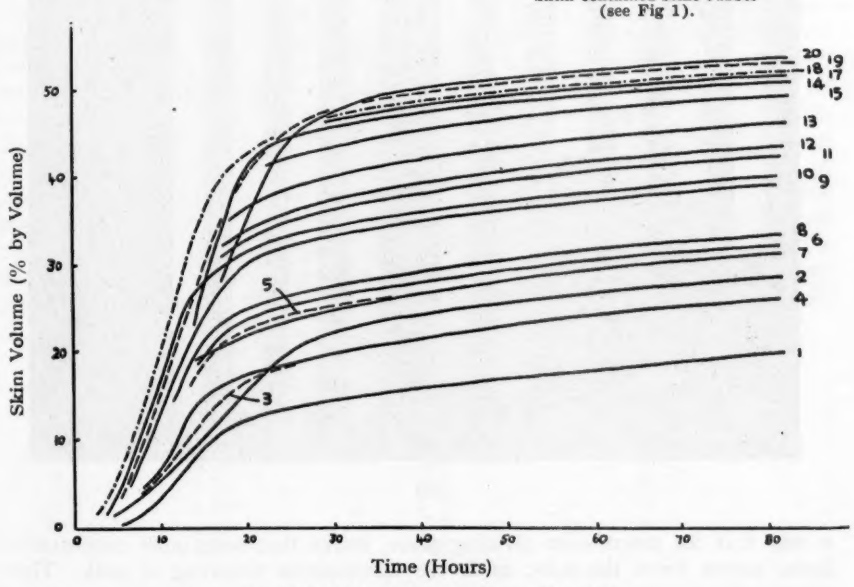

FIG. 3.—Creaming of 30% latex using sodium alginate.

Curve	1	2	3	4	5	6	7	8	9	10
Sodium alginate on aqueous phase	0.715	0.643	0.578	0.521	0.467	0.420	0.378	0.341	0.307	0.276%
Curve	11	12	13	14	15	16	17	18	19	20
Sodium alginate on aqueous phase	0.246	0.224	0.201	0.181	0.163	0.147	0.132	0.119	0.107	0.096%

Skim contained some rubber (see Fig. 1).

The different types of creaming become more obvious when latices of low rubber content, *e.g.*, 5% are creamed. Owing to the compactness of the small clusters formed with low proportions of creaming agent, and their small total volume, their migration and collection at the upper surface take place in such

FIG. 4.

a way that the cream-skim dividing plane, unlike that with more concentrated latex, moves down the tube, as in the spontaneous creaming of milk. These cream volumes often pass through a maximum. A definite creaming agent proportion, depending on the contents of rubber and of serum solids, can be determined at which this type of creaming with diluted latex changes to creaming by structure-shrinkage in which the cream-skim dividing plane moves upwards;

the creaming agent concentration at which this change in creaming-type occurs increases with decreasing rubber content and with increasing content of serum solids.

ANALYSIS OF CREAMING CURVES

Omitting those parts of the curves which represent the migration, as isolated clusters, of a minor fraction of the total rubber, it is found that rate of increase of skim-volume decreases linearly with increase of skim volumes. It is therefore possible to obtain a value for the skim volume after infinite time. Cream volume after infinite time is, in this way, found to depend linearly on proportion of creaming agent. These relationships are expressed in the equation:

$$y=(100-u-kx)[1-e^{-m(t-t')}]$$

y=skim volume after time t; x=creaming agent proportion; u=a constant characteristic of the latex (depending on rubber content but independent of the particular creaming agent); k and m are constants characteristic of the creaming agent. Values of m and k together with those of u, determined using a latex of 30% rubber content and 1.73% serum solids content, are given in Table IV.

TABLE IV

Creaming agent	m	k	u
Sodium alginate	2.54×10^{-3}	53.1	42
Methyl cellulose	3.27	41.3	41.5
Tragon A	2.33	24.6	41
Irish moss	3.51	67.9	41

The greater the value of m, the more rapid the rate of skim formation. Comparing two creaming agents at the same concentration, the one with the smaller value of k will give the more concentrated cream. The products $k.x'$, where x' represents optimum proportion, are roughly the same, about 11 to 12 for all creaming agents. Using the experimental conditions indicated in connection with Table II, the creams after infinite time using the optimum proportion of any creaming agent will be about 30 grams of rubber in (100−41.5−11.5) cc., or about 65% rubber. This value is in good agreement with that of page 453. Using methyl cellulose as the creaming agent, and a range of proportions higher than the optimum, the cream volumes formed in a 70 cm. column of 30% latex after a period of six months agree with those calculated from the equation: $y=100-u-kx$, *i.e.*, assuming t to be infinite. The results are given in Table V.

TABLE V

Methyl cellulose (% on aqueous phase)	Volume of skim expressed as % of total volume	
	(Calculated)	(Observed)
0.50	38.3	40
0.75	28.0	29
1.00	17.7	16
1.25	7.3	10
1.50	−3.0	2

Further, using the proportion which by calculation should give no skim after infinite time $\left(x=\frac{100-u}{k}\right)$ a skim volume of only 2% was obtained after a period of three months.

When skim is expressed from the initial reticular system under the buoyancy forces, this is not compressed uniformly as a whole, but a "wave" of increasing rubber content moves downwards at a rate commensurate with the upward movement of the lower level of the cream. This phenomenon can be demonstrated by experiments with a modified sedimentation tube (Fig. 5).

The upper half of a column of latex mixed with creaming agent is hydrostatically balanced against a column of water, and the change of rubber content of the top half of the column of latex followed during creaming by the difference between the levels of the latex and the water. Typical results are shown in

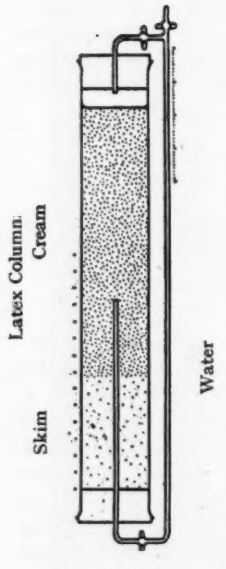

FIG. 5.—Modified sedimentation tube.

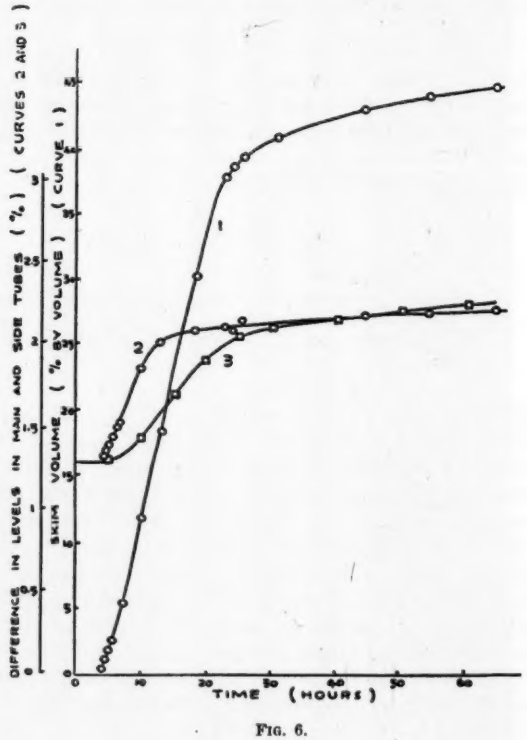

FIG. 6.

Figure 6 for a column of latex (rubber content 30%), 150 cm. long and 6 cm. diameter, containing sodium alginate (0.2% on the aqueous phase) at 21° ±2° C. Curve 3 shows the course of movement of the water in the side tube which would be expected from Curve 1 (for the relation between skim volume and time) if the rubber were uniformly distributed through the cream. Curve 2 shows the actual course and demonstrates that during creaming the rubber content is greater in the upper parts of the cream layer.

THEORY OF CREAMING

The theories which have been put forward previously to explain the creaming action of creaming agents fall into two groups, both of which assume adsorption

of the creaming agent at the rubber-water interface as the causative factor. The first group of theories suggests that adsorption of heavily hydrated creaming agent molecules results in a great increase in the effective size of the globules with almost complete elimination of the Brownian movement, so that these rise uninterruptedly under their buoyancy forces[25]. Apart from the fact that these theories disregard the clustering effect, which is here shown to be the main cause of creaming (cf. Baker[19]), the degree of hydration which would be necessary for this reduction in Brownian movement is improbable and, moreover, would hinder rather than help the effect of buoyancy. The second group of theories, based on so-called "sensitization," suggests that the creaming agent on adsorption at the rubber-water interface reduces the electric charge sufficiently to enable the globules to approach one another and to cohere loosely while at the same time enveloping them in a heavily hydrated lyosphere which prevents actual coagulation[26]. It can be shown, however, by measurement of the electrophoretic mobilities of rubber globules, that the alterations in charge by the replacement of the normally adsorbed proteins by these creaming agents are haphazard and the

TABLE VI

ELECTROPHORETIC MOBILITY OF RUBBER GLOBULES IN AQUEOUS MEDIA OF *p*H 10 AND "IONIC STRENGTH" 0.01 AT 20° C. AT THE MINIMUM CONCENTRATION FOR COMPLETE COVERING OF THE GLOBULES

Methyl cellulose	−2.5 μ/sec./volt/cm.
Irish moss	−4.5
Sodium alginate	−4
Gum tragacanth	−3
Locust bean gum	−3
Natural latex protein	−2.5
Ammonium laurate	−4.5
Ammonium stearate	−5.3
Peptone	−2.5
Starch	−3.3

charge in some cases is actually increased. The mobilities were measured ultramicroscopically in media of *p*H 10 and "ionic strength" 0.01; the rubber content was 0.03%. The results (Table VI) show also that similar changes can be brought about in the mobilities by the preferential adsorption of other surface-active substances which are also included in the table. The isoelectric *p*H values of all the creaming-agent substances are on the acid side of neutrality, and the sensitization theories are further discredited because creaming is independent of *p*H (acid latex can be creamed by the use of a suitable creaming agent[27]), and, for many, almost independent of the proportion of serum solids or other surface-active material, and a definite reproducible degree of creaming results from the use of very low creaming agent proportions.

The explanation of the mechanism by which creaming agents induce the reversible association of the rubber globules is to be found in an examination of their aqueous solution. All creaming agents are pronouncedly hydrophilic; they impart a high apparent viscosity to water and the viscosity values of the aqueous solutions decrease with increasing rate of shear. The nature of their solutions is explained by McBain[28] thus: "The apparent viscosity is due almost entirely to the presence of loose ramifying aggregates of colloidal particles united by local and specific bonds of residual affinity of different kinds and degree." In the

aqueous solutions, the hydrated molecules link themselves together (*e.g.*, by the attraction of local dipoles) into a three-dimensional network system which entraps and immobilizes the aqueous phase. When the system is subjected to a shearing stress, as when it is stirred or forced through a capillary, the network is broken down. The more slowly it is distorted, the greater is its ability to resist being broken down; hence the greater apparent viscosity the lower the rate of shear. On being allowed to rest a new network system is formed.

The theory proposed here for the associating effect of creaming agents is based on these ideas. It is suggested that creaming agent molecules, adsorbed at the surface of the rubber particles, remain capable of taking part in the formation of the loose network system of colloidal particles in the bulk of the aqueous phase. The reversibility of the cream is due to the reversibility of the aggregation of the creaming agent molecules.

When a creaming agent solution is added to latex, a number of its molecules are adsorbed at the rubber-water interface and also link up with molecules in the bulk of the aqueous phase. The first effect is a restriction of the Brownian movement of the individual globules by the anchoring effect of the network system, but their movement is not completely eliminated, and where they are separated by appreciable distances they continue to move until they come to positions when the creaming agent "links" are sufficiently strong to hold them in their relative positions. This is the mechanism of the clustering effect. Clusters grow in this manner until their buoyancy pressures are sufficient to break down the network system in the free aqueous phase. The clusters which move upwards carry with them the entrapped aqueous phase and creaming agent, but when they become a continuous layer, and the upper clusters are subjected to the compressive force of the buoyancy of those below, the layer may become more compact by expulsion of entrapped aqueous phase and creaming agent. The progress of creaming at this stage is governed by the magnitude of the compressive force and the mechanical strength of the continuous layer. The greater the proportion of creaming agent, the greater are the possible distances between the held rubber globules, and hence the lower is the proportion of globules in the clusters. With very high proportions of creaming agent, the original clusters may fill the whole space so that no creaming results.

It has been shown that clusters of rubber particles are formed almost immediately the dissolved creaming agent is stirred into the latex, but that the induction periods (p. 456) may be of several hours' duration. It is suggested that the apparent discrepancy arises because the newly formed clusters are not sufficiently great to break down the network system of the free aqueous phase and creaming commences after gradual amalgamation of small clusters to form larger ones. Within a small range of creaming agent proportions around the optimum, the clusters grow to form a substantially continuous, reticular system throughout the whole of the liquid.

The viscosity of the aqueous solutions of these substances gives a measure of the tendency of the molecules to form micellar aggregates. The views expressed above on the action of creaming agents find confirmation in that their creaming power and their ability to impart a high viscosity to water show a pronounced parallelism. Optimum proportions of various creaming agents in water give solutions of roughly the same viscosity; so also do equivalent proportions. Further, the creaming effect of mixed creaming agents is roughly additive, as is also the viscosity effect.

The anomalous behavior of methyl cellulose as a creaming agent can now be explained. In the absence of other surface-active material, adsorption of methyl

cellulose at the rubber-water or paraffin-water interface may result in the weakly polar, non-ionizing molecules lying horizontally in the interface so that the methyl cellulose molecules show merely a protective effect. The addition of another surface-active material may orientate the methyl cellulose molecules perpendicularly to the interface so that they may link up with the ramifying aggregates in the bulk of the aqueous phase, with a consequent creaming effect.

From this theory of the action of creaming agents it would be anticipated that the anomalous viscosity shown by their aqueous solutions should be shown to a pronounced degree by their mixtures with latex. The results in Figure 7 demonstrating the alteration in the apparent relative viscosity with pressure show this to be so: Curves 1-4 relate to the behavior of 30% latex containing

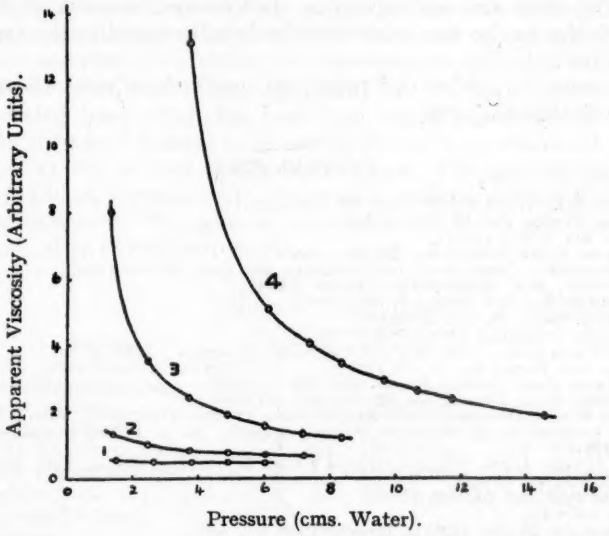

FIG. 7.

0.0, 0.07, 0.14, and 0.21%, respectively, of sodium alginate (on the aqueous phase) at 22° C. with a capillary 50 cm. long and 0.1 cm. diameter. The mixtures, moreover, possess small but definite rigidities after being allowed to stand at rest, *i.e.*, they are thixotropic.

CREAMING OR SEDIMENTATION OF DISPERSE SYSTEMS OTHER THAN LATEX

It has already been pointed out that creaming agents can induce the accelerated separation of the disperse phase in systems other than latex. Aqueous dispersions of carbon black, sulfur, titanium dioxide, fats (milk), clay and synthetic rubber (Neoprene latex), etc., can be made to separate in the same way. Incidentally the particle size of the disperse phase is of no influence on the action, because paraffin-oil dispersions of average particle size about 3μ, and Neoprene latex of average particle size 0.1μ can be treated with equal ease, although the ratio of the volumes of the average particles of the two dispersions is approximately 27000: 1.

When a suitable quantity of a creaming agent is added to a dispersion containing more than one type of dispersed substance, uniform creaming or sedimentation is the result. For example, latex containing sulfur in dispersion gives a uniform cream or sediment according to the average specific gravity of the disperse phase. Similarly mixtures of *Hevea* latex and Neoprene latex, and compounded latices generally, can be made to give uniform creams or sediments[29].

Another possible use of creaming agents with latex mixings is to ensure permanent uniformity. If, for example, latex containing dispersed zinc oxide is allowed to evaporate by exposure to the air on a glass plate, zinc oxide settles on to the plate during drying and remains there when the dried rubber film is stripped; if, however, a suitable proportion of a creaming agent is included in the mixing, no matter how slow the drying, the zinc oxide remains uniformly dispersed in the film. The effect does not depend on the increased viscosity of the aqueous phase, but is due to the zinc oxide particles being retained in the aggregates of rubber particles.

For permission to publish this paper our indebtedness must be expressed to the Dunlop Rubber Co., Ltd.

REFERENCES

[1] Weber, *Gummi-Ztg.* **17**, 652 (1903); *Ber.* **36**, 3108 (1903).
[2] Hughes, *Trans. Faraday Soc.* **29**, 211 (1937).
[3] Moyer, *Botan. Rev.* **3**, 538 (1937).
[4] Kemp and Twiss, *Trans. Faraday Soc.* **32**, 890 (1936).
[5] Bondy and Freundlich, *Compt. rend. Lab. Carlsberg, Sér. Chim.* **22**, 89 (1937).
[6] Beumée-Nieuwland, *Arch. Rubbercultuur* **13**, 555 (1929).
[7] Roberts, *J. Rubber Res. Inst. Malaya* **8**, 193 (1938).
[8] Kemp, *Ind. Eng. Chem.* **30**, 156 (1938).
[9] See, for example, Netherland Patent 38,676 (1928).
[10] See also Davis and Blake, "Chemistry and Technology of Rubber", **1937**, p. 607.
[11] Twiss, *Trans. Inst. Rubber Ind.* **6**, 426 (1931).
[12] Kemp and Twiss, *Trans. Faraday Soc.* **32**, 896, Fig. 5 (1936).
[13] Kemp and Twiss, *Trans. Faraday Soc.* **32**, 892, Fig. 1 (1936).
[14] de Vries and Beumée-Nieuwland, *Arch. Rubbercultuur* **11**, 295, 371 (1927); Bishop and Fullerton, "Latex Preservation and Shipment, Planting Manual", No. 4, Rubber Research Inst. Malaya, July, **1932**.
[15] Beadle and Stevens, *Intern. Congress Applied Chem.* **29** (1912); Stevens, *Bull. Rubber Growers' Assoc.* **5**, 216, 450 (1923).
[16] Pummerer and Pahl, *Ber.* **60**, 2152 (1927).
[17] U. S. Patent 1,678,022.
[18] Traube, *Gummi-Ztg* **39**, 434 (1925); British Patent 226, 440
[19] *Trans. Inst. Rubber Ind.* **13**, 70 (1937).
[20] *e.g.* British Patent 437,758 (1934); alkylated starch or other polysaccharide. British Patent 450,222 (1934); various hemicelluloses; aqueous extracts from straw and other vegetable matter. British Patent 448,203 (1934), British Patent 448,244 (1934) and British Patent 448,245 (1934); extracts from seeds or plants. U. S. Patent 1,994,328 (1935); water-soluble alkylated cellulose. Netherland Patent 37,288 [see also Gummi-Ztg. 51, 466 (1937)]; Konjac flour. British Patent 429,559 (1934); synthetic water-soluble polymeride homologous substances of hemi- or eucolloidal nature, *e.g.*, polyvinyl alcohol, sodium polyacrylate.
[21] Wilkins, *J. Soc. Chem. Ind.* **54**, 393T (1935).
[22] British Patent 417,162 (1933).
[23] Russell, *Proc. Roy. Soc. London* **154A**, 550 (1936).
[24] Russell and Rideal, *Proc. Roy. Soc. London* **154A**, 540 (1936).
[25] Noble, "Latex in Industry", New York, **1936**, p. 56.
[26] Stamberger, "The Colloid Chemistry of Rubber", London, **1929**, p. 30.
[27] British Patent 294,002 (1928).
[28] *J. Phys. Chem.* **30**, 239, 313 (1926).

THE CHEMISTRY OF NATURAL RUBBER

III. THE EFFECT OF AMMONIATION ON THE LATEX OF HEVEA BRASILIENSIS *

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The bulk of the liquid latex of commerce is protected against putrefaction by addition of 0.7-1.5% of ammonia. It is widely recognized that latex is profoundly affected by this procedure, but little insight has hitherto been obtained into the chemistry of the changes. The problem has now been approached by applying to latex before and after preservation with ammonia the method of analysis described in Part I (RUBBER CHEM. TECH. **10**, 1(1937)).

Ammoniated latex which has been kept under representative conditions of storage for periods of 8 weeks to 18 months differs in general in composition from fresh latex in the manner shown in the table. The quantitative findings for ammoniated latex, however, vary appreciably with the time of storage and with the ammonia content. The analysis recorded was made on latex containing 0.7% of ammonia after 18 weeks' storage.

Fraction	No.	Fresh latex		Same latex ammoniated	
		%	Description	%	Description
A. Carbon tetrachloride-acetone-soluble substances:					
Water extract	1	0.2	Crystalline	0.2	Oily
Acetone extract:					
(1) Ligroin-insoluble	2	0.1	Crystalline	0.2	Oily crystalline
(2) Ligroin-soluble	3	1.7	Oily cryst.	1.8	Non-crystalline oil
Residue *	4	3.1	Elastic solid	7.1	Viscid fluid
B. Precipitated rubber:					
Sediment	5	2.7	Crystalline	2.1	Crystalline
Water extract	6	2.9	Vitreous	1.1	Vitreous
Crude caoutchene	7	—	Soluble	—	Relatively insoluble

* The name crude caoutchol applied to this fraction in Part I is not applicable in the case of ammoniated latex (see below).

Two major quantitative changes resulting from ammoniation are apparent: the increase in amount of the residue (fraction 4) and the decreased amounts of the water-soluble fractions 5 and 6.

Qualitative changes in the components as a result of ammoniation are extensive except in the minor fractions 1 and 2.

The fractions 3, 5 and 6 are isolable from fresh latex as crystalline, readily hydrolyzable "complexes" comprising a considerable number of individual substances. The corresponding fractions of ammoniated latex consist essentially of the same materials in a more or less hydrolyzed condition. Detailed examination of these hydrolytic changes necessarily awaits a more complete knowledge of the ultimate chemical components of latex than is now available.

* Reprinted from the *Journal of the Chemical Society*, December 1938, pages 2032-2034. Preliminary work was reported in the *Journal of the Rubber Research Institute of Malaya*, Vol. 8, No. 2, pages 192-196, January 1938. (See RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 11, No. 3, pages 455-457, July 1938).

There can be little doubt that these changes affect the properties of rubber derived from ammoniated latex, but more significant from this point of view are the changes undergone by caoutchol and caoutchene. The elastic crude caoutchol (fraction 4) of fresh latex disappears on ammoniation, and its place is taken by a viscid fluid which further differs from crude caoutchol in retaining nitrogenous substances. The crude hydrocarbon component (7) is isolated from ammoniated latex in a relatively insoluble form, which retains an appreciable amount of inorganic substances. The procedure, which effects a quantitative removal of mineral-containing substances (fractions 5 and 6) from "precipitated rubber" of fresh latex (*loc. cit.*) is clearly not efficient when applied to the modified material.

Elementary analysis of the impure fractions 4 and 7 of the modified material could not be expected to throw any light on the nature of the changes, and the problem has therefore been approached by examining the behavior of the corresponding components of fresh latex, namely, crude caoutchol and crude caoutchene, under the action of dilute aqueous ammonia. Under this treatment crude caoutchol, which is normally very soluble in the usual rubber solvents, becomes relatively insoluble. Caoutchol so modified would necessarily be retained by the hydrocarbon fraction (7) during the above analysis. Crude caoutchene from fresh latex undergoes a complex change in contact with dilute aqueous ammonia. Solubility evidence indicates that a small portion of it is disaggregated, and the major portion reaches a higher degree of association than is found in the naturally occurring product. The same change doubtless takes place in ammoniated latex, with the consequence that the disaggregated portion, in virtue of its increased solubility, appears, together with associated nitrogenous substances, as the residue (4). The diminution in solubility of the main hydrocarbon fraction is intensified by the presence therein of the modified caoutchol; the observed retention of some mineral-containing substances by this mixture under the conditions of analysis is readily understood.

EXPERIMENTAL

The differing characteristics of fresh and ammoniated latex and of certain of their components make necessary the use of somewhat different analytical procedures in the two cases.

Analysis of Fresh Latex.—The latex (100 g.), the total solid content of which is determined, is evenly distributed over a sheet of plate glass approximately 50 cm. square and is dried at 45-50° (1-2 hours). The resulting film is added in strips to a mixture of carbon tetrachloride (14 vols.) and acetone (9 vols.) (115 cc. of mixture for each 3 g. of dried film) and is kept in subdued light with occasional stirring for 24 hours. The homogenous dispersion is then treated with a volume of acetone equal to that already used (45 cc. for each 3 g. of dried film). The further procedure is as described in Part I (*loc. cit.*).

Analysis of Ammoniated Latex.—The viscosity of ammoniated latex is low relative to that of fresh latex, and it is convenient to dry 100 g. of the liquid by distributing 50 g. on each of two plate-glass sheets 50 cm. square.

The dried film from ammoniated latex does not form a homogeneous dispersion in the carbon tetrachloride-acetone reagent. To ensure complete extraction of soluble substances from the dried film, the mixture is kept with occasional stirring for at least 48 hours before being treated with the precipitant. The remaining procedure is in general as usual; but the diminished solubility of the main hydrocarbon fraction of ammoniated latex may render the isolation of the

sediment from the "precipitated rubber" by centrifugation impracticable. In this event the dispersion of the "precipitated rubber" in benzene is immediately subjected to the treatment with water. The water-soluble sediment and the water extract will thus be isolated as a single fraction (5+6. See Table).

The ammoniated latices examined had been stored either in the dark (metal drums) or in diffuse daylight (glass vessels). Neither diffuse daylight nor the type of container has been observed to affect the results of analysis.

Observations on the Components.—Fraction 1. Isolated from ammoniated latex, this material is completely soluble in ethyl alcohol and is therefore free from quebrachitol, but is otherwise indistinguishable from the corresponding fraction of fresh latex.

Fraction 2. Changes produced by ammoniation are of minor interest and have not yet been studied.

Fraction 3. The material isolated from fresh latex readily crystallises when kept (See *J. Rubber Res. Inst. Malaya,* **8**, 181 (1938)), and is an ester-complex which is readily hydrolyzed by alcoholic potassium hydroxide but not by cold dilute aqueous alkali. The corresponding material from ammoniated latex is an oil, uncrystallizable at room temperature. Extraction of the oil with light petroleum in presence of cold dilute aqueous alkali separates it into acidic and alcoholic fractions, the investigation of which is in progress.

Fraction 4. This elastic, hydrolyzable component of fresh latex (crude caoutchol; *loc. cit.*, p. 224) is ash- and nitrogen-free. The corresponding viscid fraction of ammoniated latex is ash- and quebrachitol-free, but contains nitrogen (Found: N, 0.3%). It gives no evidence of being saponified when heated for 1 hour with 1% aqueous sodium hydroxide.

Crude caoutchol (20 g.), isolated from 2 l. of fresh latex, was added in the form of a thin sheet to water (2 l.) containing 0.7% by weight of ammonia, and the mixture was kept for 8 weeks with intermittent shaking. In this way the concentrations and storage period for typical ammoniated latex were closely imitated. At the end of the period the aqueous liquor was pale yellow and almost clear, and frothed when shaken. From it was isolated a small amount of a complex mixture of organic acids, including the sulfur-containing component of crude caoutchol mentioned in Part II (RUBBER CHEM. TECH. **11**, 445 (1938)). The insoluble portion of the reaction mixture was opaque, cream-colored and spongy. Washed, passed through the closed rolls of a mill and dried in a vacuum, it was a highly elastic, tough, yellow substance, insoluble in ether and only very slowly dissolved by the usual rubber solvents.

Fractions 5 *and* 6. These mineral-containing fractions of fresh latex, after being heated for 30 minutes with 3N-sulfuric acid, both give normal positive reactions with ammoniacal silver nitrate, Fehling solution and ammonium molybdate. The untreated materials on the other hand do not reduce Fehling solution, and do not give normal reactions with ammoniacal silver nitrate or with ammonium molybdate. Both materials contain small amounts of nitrogenous substances (ninhydrin) (Found for fraction 5: N, 0.5; for fraction 6: N, 3.5%). Fractions 5 and 6 of fresh latex thus consist of "complexes" comprising reducing substances, nitrogenous substances and mineral phosphates (for the cations of latex, see Rae, *Analyst,* **53**, 330 (1928)). The corresponding untreated fractions of ammoniated latex give normal positive reactions with the above reagents.

Fraction 7 (*crude caoutchene*). Isolated from fresh latex, this material is readily soluble in the usual rubber solvents and is virtually ash-free. The corresponding material from ammoniated latex burns with an appreciable ash and is

difficultly and incompletely soluble. Both forms retain the bulk of the nitrogenous matter of latex (Found for caoutchene of fresh latex: N, 0.4; for caoutchene of the same latex after 4 weeks' ammoniation: N, 0.4%).

Crude caoutchene from fresh latex was treated with dilute aqueous ammonia in the same manner as crude caoutchol (see above). After 8 weeks the ammoniacal liquor contained only a negligible amount of dissolved solid substances. The caoutchene, after being washed, sheeted and dried in a vacuum, was obtained as a tacky, light brown product, a portion of which was readily dissolved in 3-4 hours by the usual rubber solvents. The decanted clear solutions contained small amounts of viscid, semi-fluid material. The major, undissolved portion slowly swelled in the solvents, but remained to a large extent undissolved by benzene, carbon disulfide, ether and ligroin even after 24 hours. A higher degree of dispersion was observed in chloroform, carbon tetrachloride and toluene, but in these media also, solution was incomplete in 24 hours.

I am indebted to K. C. Sekar for the nitrogen determinations, and to the Director of this Institute for permission to publish the results of the investigation.

SPONTANEOUS COAGULATION OF RUBBER LATEX *

PAUL STAMBERGER

MALAYA

As early as 1913, Whitby advanced the view that spontaneous coagulation in rubber latex takes place before decomposition processes begin[1]. Arguments against this view have since been advanced by several investigators, and the opinion generally held at present is that the coagulation of fresh latex is caused by formation of acid from the bacterial decomposition of the serum components.

Recent investigations made on latex of *Hevea brasiliensis* have provided confirmation of the view held by Whitby. Experiments were conducted throughout on latex obtained immediately after collection from the trees, which had been tapped three or four hours previously. The formation of ions from decomposition of latex was followed by conductivity measurements. The conductivity of latex did not change until coagulation was complete. This occurred 6-11 hours after collection of the latex, varying from sample to sample. The resistance of the conductivity cell increased after gel formation, due to contact resistance on the electrodes.

The *p*H after coagulation (measured by Lyphan indicator strip) was only 0.2 lower than the average original figure of about 6.4. Decreasing the *p*H below 6 by the addition of phthalate-KOH buffer solutions had no effect on the rate of coagulation of the samples. After coagulation, decomposition of latex components proceeds; but this bears no relation to the process of coagulation which is already complete.

Further support of Whitby's view was provided when strong antiseptics preventing bacterial decomposition were added to fresh latex without preventing spontaneous coagulation. The addition of 0.3 and 0.4 per cent of sodium pentachlorophenate had no influence on the behavior of latex as described. No decomposition or any change in the *p*H value of 7 could be found in coagulated samples which were measured over a period of 3-6 weeks.

The exact nature of this process of coagulation is not known; enzymatic action on proteins may, however, be put forward as an explanation.

REFERENCE

[1] *Kolloid-Z.* **12**, 151 (1913).

* Reprinted from *Nature*, Vol. 143, No. 3621, page 520, March 25, 1939.

COMPOSITION AND COLLOIDAL PROPERTIES OF BALATA LATEX *

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INTRODUCTION

Balata is derived from the latex of trees of the *Mimusops*[1] tribe in the *Sapotaceae* family. The *Mimusops* include a large number of species of evergreens having a wide distribution in the tropics but concentrated in the Amazon and Orinoco river basins and in the Guianas.

Although balata has been an important commercial raw material for over fifty years, almost nothing has been published concerning the chemical composition and properties of its latex. Due to the wide interest prevailing in *Hevea* latex, it was felt that a study of a kindred latex such as that of balata might reveal information of general interest to rubber technologists. Specifically it should be of considerable interest to colloid chemists to compare the properties of balata latex with those of *Hevea* latex.

Balata latex, unlike rubber latex, does not appear to have been used commercially as such, and has therefore not been easily available for study. About six years ago the author obtained about one gallon of each of two balata latices tapped from two types of "bullet trees" used in making Surinam sheet balata. These samples were collected under the direction of the Balata Company, Surinam, and sent to us directly from Paramaribo through the agency of Weise and Company of Rotterdam, whose assistance we gratefully acknowledge.

Hauser[2], who examined balata latex microscopically, states that there are two kinds of the so-called "bullet tree." One has a round fruit and yields a bitter reddish latex containing considerable tannin, whereas the other has an oval fruit and gives a mild white milk which is preferred for making good balata.

One of the balata latices received from the Surinam Company fitted Hauser's description of a white latex except for its faint pink color and will be designated as "white." The other one which had a pronounced reddish color will be designated as "red."

Since several weeks had elapsed between the time the latices were gathered and their delivery, some fermentation had set in, as evidenced by the presence of carbon dioxide, alcohol and acetic acid. It appears that this fermentation resulted from the presence of natural sugars contained in the latex which were acted on by the bacteria from the air. Both samples were acid to litmus and had an ethereal odor. A sour cheesy odor was also noticeable in both latices, being stronger in the case of the red. However, this odor was not particularly unpleasant compared with the bad odor of *Hevea* latex on fermentation. The samples contained some small pieces of bark, but were otherwise clean, and were practically free from clots. Both had the consistency of thick cream, the red latex being somewhat thicker than the white variety, in spite of having a lower content of solids.

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 16, pages 68-79.

Our study was made on these latices after they had been carefully strained through a fine gauze to remove pieces of bark and other adventitious impurities which had dropped in during tapping. The strained latices were kept thereafter in glass bottles in an electric refrigerator at about 5° C. except when removed to take samples. Under this condition the white latex has remained in perfect dispersion for over six years while the red latex gradually coagulated on the surface. After six years the *p*H value of the white latex was 3.6.

PHYSICAL CHARACTERISTICS

Hauser[2] made a microscopic study of balata latex and found that the latex particles were spherical and varied from 0.5 to 3.5 microns in diameter, with particles less than 0.5 micron observable in the ultra-microscope.

F. F. Lucas of these laboratories has examined the two balata latices herein described, employing the ultra-violet microscope and technique recently described by him in a study of *Hevea* latex[3]. Lucas has kindly furnished the author with

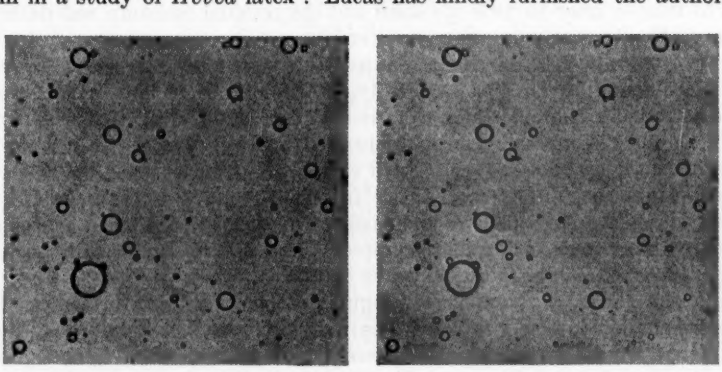

FIG. 1.—Balata latex particles, ×1800; showing two optical sections 0.25 micron apart, taken with ultra-violet microscope, Cd λ 2573 Å.

the photomicrograph shown in Figure 1, which confirms Freundlich and Hauser's findings that the particles are perfect spheres. In a preliminary investigation Lucas found the particle size to range in diameter from about 0.1 to 2.5 microns, and the average particle size in both latices was found to be about 0.5 micron. It is possible that some particles may exist which are less than 0.1 micron in diameter, since this is about the limit of the equipment employed by Lucas. Under the ultra-microscope there appear to be a multitude of particles which exhibit very lively Brownian motion, whereas the larger particles are in only faint motion, which is true also in the case of *Hevea* latex.

As a result of micro-manipulation studies, Hauser[2] concluded that the balata latex particles have a tough skin and a fluid center. He states that there are many indications that there is an adsorbed layer of resins on the membrane.

The extracted resin of washed and dried balata is a viscous sticky liquid and constitutes 40 to 50% of the material, yet the balata is not sticky at ordinary temperature. This is taken as evidence that the resins are not adsorbed on, but are located within the latex particles. Further evidence that the particles contain the resin is adduced from measurements of the density of white balata latex. Accurate density measurements cannot be made without considerable dilution of latex, owing to the difficulty of removing air bubbles. When diluted to solids

contents of 11.3 and 5.88%, accurate density determinations were made at 20°/4° C. using a pycnometer. The values found were 0.9982 and 0.9983, respectively, for the above dilutions, showing that the density of balata latex remains practically constant on dilution. This can be explained by the fact that the volumes of serum and balata particles are practically equal in the original latex. Since the density of serum-free dry balata at 20° C. has been found to be 0.975, the density of the serum must be about 1.025 to compensate. Therefore, as the latex is diluted the density of the serum decreases, and the increase due to the fewer particles present compensates for this loss.

PARTICLE COMPOSITION

The balata particles, besides containing hydrocarbon and resin, appear also to contain considerable water. The water content has been determined in balata, coagulated from the latex with alcohol and the alcohol quickly removed upon washing with warm water. The washed coagulum was then pressed to a thin sheet to remove inter-particle moisture and the residual moisture was determined by the method recently described by Kemp[4].

In two separate determinations the moisture contents determined on the dry basis were found to be 18.7 and 18.1%. Although it is not proved that the particles actually contain this water within their outer shell, this would not be surprising, since sterols are known to swell strongly in contact with water. The author believes this moisture to be held within the particles since the washed and pressed balata coagulum is practically free from water-absorbing impurities on the outside of the particles and the surfaces of the particles must be in perfect contact without voids. For a more complete discussion of this matter the author's recent article[4] on *Hevea* latex should be consulted.

From the above considerations it appears that sheet balata has a particle structure similar to sheet rubber. The individual particle structures, however, are different since the rubber particles are made up of sol and gel phases, whereas balata hydrocarbon is more crystalline and does not contain phases of different solubilities in solvents. Furthermore the resin content of the balata particle is about 40% of the whole, while the *Hevea* particle contains only about 1% acetone-soluble matter[4].

It is of interest to consider the exact location of balata resin in the particle. In this connection it is possible to wash balata for hours under hot water while it is very plastic, following which treatment it has not become sticky, indicating that resin has not been dislodged from the particles as it probably would have been if it were present as a liquid in the center of the particle. It would indeed be remarkable if balata could be mechanically worked under hot water without rupturing the particles. Since the plastic temperature of balata is about 60° C. and that of the hydrocarbon at least 30° C. higher, it would appear that the resin components must at least in part be dissolved in the hydrocrabon to lower its softening temperature. The greater hardness of the hydrocarbon as compared with the balata also indicates that the resin is either dissolved in or homogeneously dispersed in the hydrocarbon.

Hevea and balata latices appear to have certain features in common. These latices are suspensoids, the particles of which are composed of hydrocarbon and sterol substances and vary in diameter from about 0.1 to 2.5 microns, with the maximum number of particles in the lower range. The latex particles contain water and have a protective substance or substances adsorbed on their surfaces. In the case of *Hevea,* the particles contain a strongly adsorbed protein, while

the adsorbed protective layer on balata globules can be removed by washing. The serums contain salts proteins, amino acids, sugars and many other substances less well defined, which are present to the extent of 10 to 15% based on the total solids. The function of these numerous substances in the plant metabolism is not understood. The chemist therefore has much to learn regarding the mechanism of plant synthesis in the production of these useful latex products.

CHEMICAL ANALYSIS

Table I gives the results of chemical analysis of both latices in comparison with the normal range of composition of prime amber sheet balata. These data indicate that prime amber is a product of mixed latex from both types of trees, with the white latex predominating. The white latex is superior to the red on account of its distinctly higher hydrocarbon content and gutta/resin ratio, which is in accordance with the statement of Hauser[2].

TABLE I

ANALYSES OF BALATA LATEX AND PRIME AMBER SHEETS

	White latex		Red latex		
	% based on				
	Latex	Solids	Latex	Solids	Prime amber
Total solids	55.4	—	45.9	—	—
Water and volatile matter at 100° C.	44.6	—	54.1	—	2–5
Resin (cold petroleum ether extract)	20.6	37.1	20.0	43.6	37–40
Hydrocarbon (solvent extraction)	29.5	53.3	19.6	42.8	46–52
Ratio gutta/resin	1.43	1.43	0.98	0.98	1.0–1.3
Water-solubles and dirt	5.3	9.6	6.3	13.6	10–15
Ash	0.43	0.77	0.49	1.08	—
Nitrogen (Kjeldahl)	0.27	0.49	0.39	0.85	0.5–0.7
Acidity (cc. normal NaOH per 100 cc. of latex)	9.0	—	10.0	—	—

QUALITY OF BALATA FROM DIFFERENT LATICES

Sheets of balata were made from white and red latex, by drying over calcium chloride in the dark at room temperature, for comparison with first-quality Dutch and British sheet. The latex sheets were light amber in color, turning red on long exposure to air and to a deep red on exposure to sunlight. This probably explains the presence of light and dark sheets in commercial lots, since in some cases sunlight exposure may be involved in their preparation. The quality of the washed and deresinated balata hydrocarbon from both latices appeared to be about the same. Each had a tensile strength of about 5,000 lbs. per sq. inch, with an elongation of about 450% at break, using dumb-bell specimens. About the same values were obtained in the case of hydrocarbon from Dutch prime amber and British sheet. This would indicate that considerable care is exercised in preparing the prime balata sheet of commerce and that very little if any inferior gums are added as adulterants. Relatively little dirt is found in the best grades of balata, compared with gutta-percha of the jungle variety.

SERUM SUBSTANCES

Tschirch and Schereschewski[5] found commercial sheet balata to contain 0.96% ash and 5.7% water extract. By precipitation with tannic acid they separated

albuminoids from the serum, and by precipitation with alcohol a gum which gave reactions for carbohydrates. Spence and Kratz[6] separated the insoluble matter from balata and found it to be a complex of protein and carbohydrate.

We were able to extract 9.88 and 10.01% water-soluble matter from samples of two lots of prime amber sheet balta. Sheet balata is the result of drying the entire balata latex as is the case for the solids described in Table I. In both cases it appears to be possible to extract practically all of the serum substances with water. It can be stated also as a matter of experience that commercially well washed balata is practically free from ash and nitrogenous substances.

When balata latex is diluted with water and coagulated by adding 95% ethyl alcohol up to about 40% concentration, practically all of the serum substances are found in the alcohol solution. This solution is cloudy due to an incipient precipitation of some of the protein present, which can be filtered off leaving a clear brown coloured solution. On adding alcohol up to about 80% concentration in this solution, a substance giving carbohydrate reactions is precipitated. A small amount of residual nitrogenous substances remains dissolved in the 80% alcohol filtrate. This filtrate on evaporation deposits a reddish gummy substance high in ash content and present to the extent of about 2% in the original latex. This substance has a bitter astringent taste and gives a strong Benedict reaction for sugar. The reddish color in balata latex is believed to be due to tannin substances, since the presence of tannin is indicated in the serum of both latices by the ferric chloride test. Tannin, however, is believed to be a contaminant of the latex coming from the bark of the balata tree, which is rich in tannin. The amber to red color of balata sheets is probably the result of the presence of tannin which darkens on exposure to air and light as a result of oxidation. Balata sheets which are dried out of contact with strong light have a light tan color which slowly turns to amber on standing. Tappers try to avoid contamination with tannins from the bark in producing the desirable light-colored product.

The ash components are found in the latex serum. No reference has been found giving the composition of balata ash. Since its composition suggested the presence of certain components in the serum, a complete analysis was made of it. About 50 grams of dry white balata latex solids were ashed by the A.S.T.M. method D-297-36. The almost white ash is composed of oxides and carbonates together with some sulfates and chlorides of several elements. A spectrochemical analysis was made to determine the positive elements present. The remaining ash was treated with sulfuric acid to render the silica insoluble and convert the oxides, carbonates, and chlorides to sulfates. A quantitative analysis was made to determine the silica and the major elements present as sulfates. These elements are reported in Table II as oxides on the basis that the original ash contained only oxides. This is done in order to compare these results with the only comparable ones available in the literature on the ash of evaporated *Hevea* latex as given by Bruce[7]. Reference to the tabulated analyses shows a wide difference between the composition of balata and *Hevea* ashes, although the total ash contents of balata and *Hevea* latices are about the same. The analyses indicate that balata latex contains relatively little phosphorus in comparison with *Hevea*, which is known to have a high phospholipide content. The absence of phospholipides in balata is indicated also by its practical freedom from fatty acids. The very high base content and especially the high alkaline earth content are notable. In view of this one might expect to find the natural *p*H of the balata latex to be high. Fermentation, which formed acids, prevented us from determining this *p*H, and no value was found in the literature for freshly tapped balata latex.

TABLE II

ANALYSIS OF ASH FROM BALATA LATEX

	Evaporated Balata latex %	Evaporated *Hevea* latex (Bruce) %
CaO	26.92	8.7
Na_2O	24.63	12.4
MgO	21.33	5.8
K_2O	20.78	43.0
SiO_2	4.66	—
P_2O_5	0.98	24.0
Al_2O_3	0.45	—
Fe_2O_3	0.25	—
SO_3	—	2.8
Cl, CO_2, and Fe	—	0.7
	100.00	97.4

Note.—Other elements found spectrochemically in balata ash are Li, Sr, Pb, Sn, Rb, Zn, Ba, Cu, Mn, and Ni. Ramage[8] states that rubidium is found widely distributed in soils and plants.

BALATA RESIN

Gutta-percha and balata resins have been shown by several investigators to consist essentially of mixtures of sterols and sterol esters. The resins found in the gums from the different members of the *Sapotaceae* family vary from liquids to solids, and the amount present in the several species varies widely.

To obtain the balata latex resins in pure form free from serum substances, the latices were coagulated with 95% alcohol, and the coagulum washed with 40% alcohol and dried. The resins were then extracted with cold ethyl ether, 42% being removed from the white latex coagulum and 51% from the red. Both resins were water-white viscous liquids, the red latex product being slightly elastic and more viscous than the white. Table III gives the results of tests on these resins compared with those obtained on the yellow liquid resin which is a by-product of deresinating prime amber sheets. Like the commercial resin, both latex resins deposit crystals on standing. These crystals are mixed esters, which are practically insoluble in cold alcohol, and are composed in part of the acetate of β-amyrin ($C_{30}H_{50}O$); β-amyrin is a terpene alcohol with needle-like crystals, m.p. 197° C., whose chemical constitution has not been fully determined[9]. Both balata and gutta-percha resins consist of complex mixtures of terpenes, alcohols and esters, which are very difficult to separate in pure form and whose structures have not been elucidated. These substances are chemically unsaturated and show optical activity. They appear to be closely related to the sterols.

The solubility in cold and hot alcohol has for many years been used to separate gutta-percha and balata resins into two fractions, the so-called fluavile (soluble portion) and albane or insoluble fraction. Since both the fluavile and albane portions are mixtures of several substances, the solubility depends on the ratio of alcohol to resin taken, as well as on other variables in the experiment. This characterization is therefore only a crude one. The alcohol-soluble fraction is larger in balata resin than in gutta-percha resins, indicating a lower content of the high-melting sterol esters in balata. It is to be noted from Table III that the solubility of the white balata latex resin in cold alcohol is considerably higher than that from the red latex. The iodine value and refractive index of the white latex resins also differ somewhat from the values found in the case of the red latex resin.

No exhaustive research was undertaken to separate and positively identify the different components in these resins. By fractional solution methods one finds

that these resins consist of a mixture of several substances, varying from liquids to solids of widely varying melting points but all giving tests for sterols. Balata albanes present in the crystalline portion insoluble in cold alcohol have been shown by Cohen[11] and by Tanaka, Kuwata and Suzuki[12] to contain β-amyrin acetate, m.p. 230-1° C. ($C_{32}H_{52}O_2$), and an ester of lupeol, m.p. 195-6° C. We have noted butyric and caproic acids, in addition to acetic acid, in the saponifiable fraction of the resin. The unsaponifiable fraction which constituted the major part of the resin appears to be a complex mixture of sesquiterpenes and their alcohols.

Little is known regarding the function of these sterol substances in the plant metabolism. It should be remarked, however, that the close structural relationship of these sesquiterpene compounds to isoprene indicates that they may play an important role in the hydrocrabon synthesis by the plant.

TABLE III

ANALYSIS OF BALATA LATEX RESINS

	White latex	Red latex	Prime amber
Acid number	0.0	0.0	0.9
Saponification number [a]	82.3	82.7	55
Iodine values (Wijs)	158.0	137.7	158
Refractive index at 20° C	1.5187	1.5257	—
Salkowski and Liebermann tests	Positive	Positive	Positive
Solubility in cold 95% alcohol % [b]	82.2	36.0	—
" " hot 95% " "	100	100	—
Separated on cooling alcohol, %	8.4	3.5	—

[a] Berry[10] gives the saponification value of balata resin as 69.2.
[b] 2 g. resin and 15 cc. 95% alcohol after standing 48 hours at room temperature.

BALATA HYDROCARBON

Although balata hydrocarbon is known to be chemically and structurally identical with gutta-percha hydrocarbon, it must be recognized that important differences may exist in the mechanical properties of gutta hydrocarbon from different sources. The hydrocarbons from some of the lower grade guttas or balatas are often of lower strength, which may be the result of a lower state of polymerization, but more likely is because they have suffered from oxidation. Much more study of the hydrocarbons obtained from the latices of different species must be carried out to determine differences which may exist.

We have separated the balata hydrocarbon in a high state of purity from both latex and fresh prime amber sheet and have determined some of its constants, which are given in Table IV[13].

Dean[14] gives the density of gutta hydrocarbon as 0.945 to 0.955, but does not mention the temperature at which it was determined. We have determined the specific gravity of pure gutta hydrocarbon from different sources and find it to vary from 0.960 to 0.963 at 20° C. Our dielectric constant value agrees well with that of 2.45 given by McPherson[15]. It should be noted that small amounts of oxidation products and residual resins increase the dielectric constant of gutta hydrocarbon.

Kirchhof[16] gives the refractive index of gutta-percha hydrocarbon at 42° C. as 1.5180, which is slightly higher than our value at this temperature. Messenger[17] gives the heat of combustion as 10990 cal./g. for gutta-percha hydrocarbon and 11000 cal./g. for balata hydrocarbon. It should be noted that he made corrections

for impurities present due to the fact that his hydrocarbons were not pure. His separate determinations showed variations as high as 450 cal./g., which is excessive for this type of determination. We did not apply a correction factor, as our material was of a high degree of purity as determined by combustion analysis, iodine value and its freedom from ash and nitrogen. Our values on two samples of pure balata hydrocarbon were 10799 and 10801 cal./g., which is better agreement than is ordinarily to be expected.

The value of 10800 cal. g. for the heat of combustion of gutta or rubber hydrocarbon is probably very close to the true value, since it corresponds closely to the published values for several terpene hydrocarbons which are isomeric with gutta and rubber hydrocarbons. Palmenberg reported values of 10837 and 10800 cal./g. for the heats of combustion of pure sol rubber hydrocarbon which we have extracted from resin-free crepe rubber by the cold petroleum ether diffusion method. The value for rubber hydrocarbon reported by Messenger[17] was 10970 cal./g. Kirchhof and Matulke[18] reported a value of 10700 cal./g. for acetone-extracted crepe. This value is low, owing to the presence of protein and ash

TABLE IV

PROPERTIES OF BALATA HYDROCARBON

Softening temperature (Obach's method)	60–61° C.
Specific gravity at 20° C.	0.961
Dielectric constant (1000 c.p.s., 25° C., mercury electrodes)	2.40
Refractive index n_D^{33}	1.5370
n_D^{20} (extrapolated to 20° C.)	1.550
Heat of combustion (cal. per g.) [a]	10800

[a] Calorimetric tests were conducted by the Oscar W. Palmenberg Laboratories, New York City. The procedure was to use an Atwater-Mahler gold-lined calorimeter standardized with benzoic acid. Temperature readings were made on differential Fuess thermometers reading over a range of 5° C. using a lens giving readings to 0.001° C. Heat loss or gain during the operation was determined by Regnault-Pfaundler formula. Corrections were made for heat of combustion of ignition wire and acidity due to sulfur or nitrogen which may be present. Thermometers were standardized by the Physikalisch-technische Reichsanstalt, Charlottenburg, Germany. Quantity of substance was chosen so that the heat rise lay between 3° and 3.5° C. so as to increase accuracy.

left in the crepe rubber after this treatment. More recently Jessup and Cummings[19] obtained a value of 10802 cal./g. for ether-soluble rubber hydrocarbon.

Pure balata and gutta-percha hydrocarbons are milky-white at room temperature due to inner crystallization. When heated to about 70° C. the crystals melt and the hydrocarbon becomes crystal clear. On cooling at about 1° C. per minute the hydrocarbons start to crystallize at about 37° C. and the mass becomes quite opaque at about 33° C. It would appear from these observations that the β-hydrocarbon which crystallizes out under these conditions has a melting point of 37 to 40° C. Super-cooling, however, may have occurred, making this melting point too low.

The refractive index of balata hydrocarbon was measured at different temperatures during slow cooling between 70° C. and 33° C. The refractive index, however, could not be determined with accuracy below 33° C. because of opacity. Pure gutta-percha hydrocarbon from Goolie Soondie gutta-percha gave almost identical results. The refractive index data for these two hydrocarbons are given in Table V and are plotted in Figure 2. In the case of the gutta-percha hydrocarbon it was possible to determine the refractive index value at 27° C. The extrapolation to 20° C. is therefore shorter than for balata hydrocarbon, giving 1.550 as the proximate value for the refractive index of gutta-percha and balata hydrocarbons at 20° C.

It appears that the refractive index of amorphous gutta hydrocarbon between 70° and 37° C. changes with temperature at about the same rate as rubber hydrocarbon between 70° and 20° C. The β-gutta appears to have a different refractive index from the amorphous material. A further study of the refractive properties of gutta hydrocarbon as affected by crystallization should be made.

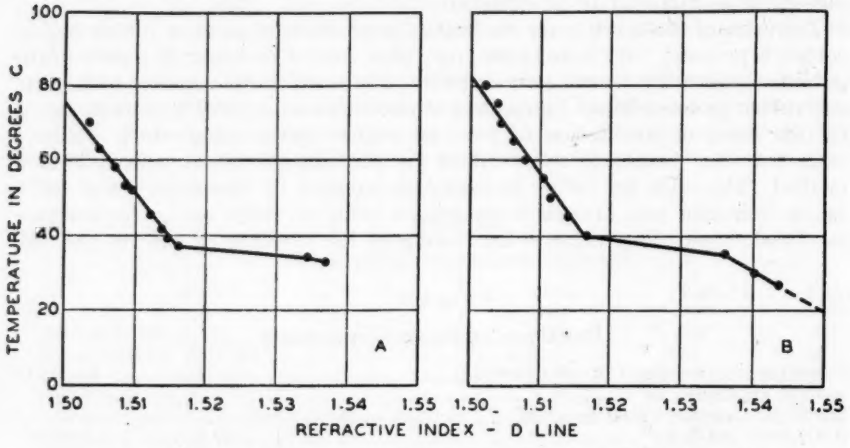

FIG. 2.—Effect of temperature on refractive index, A—Balata hydrocarbon and B—Gutta-percha hydrocarbon.

TABLE V

EFFECT OF DECREASING TEMPERATURE ON REFRACTIVE INDEX OF GUTTA-PERCHA AND BALATA HYDROCARBONS [a]

Balata hydrocarbon		Gutta-percha hydrocarbon from Goolie Soondie	
Temp. ° C.	Refractive index	Temp. ° C.	Refractive index
70	1.5033 clear	80	1.5020
63	1.5050 "	75	1.5038
58	1.5070 "	70	1.5045
53	1.5086 "	65	1.5060
52	1.5095 "	60	1.5080
45.5	1.5121 "	55	1.5105
41.5	1.5135 "	50	1.5118
39	1.5146 "	45	1.5138
37	1.5163 "	40	1.5167
34	1.5345 slightly opaque	35	1.5360
33	1.5370 very opaque	30	1.5402
		27	1.5430

[a] Thin strip of gutta pressed between heated prisms of an Abbé refractometer and slowly cooled.

We have noted, for example, that the transformation of the β-gutta occurs at a higher temperature than 37° C. if the temperature is gradually increased from 20° to 70° C. The effect of keeping the temperature constant at various temperature intervals was not studied. It should be possible by more work along these lines to obtain additional information regarding the crystalline modifications of gutta hydrocarbon which have already been studied to some extent by x-ray and electron diffraction methods.

COLLOID PROPERTIES

The unusual stability of balata latex sharply differentiates it from *Hevea* latex. Unlike *Hevea* it is not coagulated by the addition of dilute acids and alkalies or salts. Both latices cream on standing, the addition of electrolytes increases the rate of creaming, but the cream can be easily redispersed by shaking. The addition of acetone or 95% alcohol is the only satisfactory procedure now known for bringing about coagulation. The addition of 50% alcohol does not bring about coagulation. When it is desired to remove serum substances a satisfactory coagulation procedure is to dilute the latex with two or three times its volume of distilled water and add 95% alcohol slowly with stirring. Coagulation starts after about 10% by volume of alcohol has been added and is complete after about 40% addition. At the final stage the balata separates and almost completely fills the vessel with a spongy coagulum from which the occluded serum can be easily removed by pressing.

Stevens[20] and Daniel, Freundlich and Söllner[21] have recently reported on the unusual stability of a *Mimusops* latex from Brazil, which they call Abiarana gutta-percha latex and classify as *Lucuma lastiocarpa*, family *Sapotacea*. This appears to be the same product as that described by Van der Laan[22] as Abiarana, which also was collected in Brazil and found to contain as high as 95% gutta-percha. The high hydrocarbon and low resin content of Abiarana described by Stevens marks this as an unusual latex, which has a composition much nearer to the *Palaquium oblongifolium*, Burk. gutta-percha than to the *Mimusops* balata species.

Stevens pointed out that the great stability of Abiarana latex must be due to some protective substance contained in the latex. Daniel and his coworkers concluded that this protective substance is reversibly adsorbed on the particles and that it has a high molecular weight, since it cannot be removed from the latex by dialysis. Addition of an equal volume of Abiarana latex to *Hevea* latex was found to protect the rubber completely from coagulation when an excess of acetic acid was added. These authors, however, were unable to determine the chemical nature of this protective substance, but concluded that it was not a protein.

We have found that balata latex also contains a similar protective substance in its serum. Rubber latex, to which is added an equal volume of balata latex does not coagulate with acetic acid. The unusual protective power of this serum component is a matter of considerable interest, since no other substance is known which has an equal stabilizing influence on rubber latex.

SUMMARY AND CONCLUSIONS

This paper reports the composition and colloidal properties of two types of balata latex from Dutch Guiana. The white variety is shown to be superior to the red, owing to its higher content of hydrocarbon.

It is shown that balata latex is very stable due to the presence of a highly protective water-soluble substance in its serum. It cannot be coagulated by acids or salts but is readily coagulated by alcohol or acetone.

The balata latex particles are spherical and vary in diameter from about 0.1 to 2.5 microns with an average diameter of about 0.5 micron.

The balata latex particles are shown to enclose the resins, which appear to be present in a dispersed state in the hydrocarbon. The particles are shown to contain about 18% of water, determined as water of retention in pressed coagulum.

The "resins" have been separated from both types of balata latex as water-white viscous liquids, which deposit crystals of β-amyrin acetate on standing. The red balata latex resin is shown to be more viscous than the white and to differ from it as regards its iodine value, refractive index and solubility in cold 95% ethyl alcohol.

The serum components have been separated into four main fractions: protein, carbohydrate, gummy substance and ash. Minor components such as tannin and amino acid have also been noted.

A complete analysis of balata ash has been made and compared with the analysis of ash from *Hevea* latex by Bruce. Balata ash was found to contain higher contents of CaO, Na_2O, and MgO and lower contents of K_2O and P_2O_5 than *Hevea* latex ash.

New data are presented on the density, refractive index, dielectric constant and heat of combustion of balata hydrocarbon which are believed to be more reliable than similar data previously available in the literature. Data on the effect of temperature on the refractive index of balata and gutta-percha hydrocarbons are presented, showing the crystallization of the gutta hydrocarbon on cooling, which starts at about 37° C. resulting in an abrupt increase in refractive index occurring between 37° and 35° C.

ACKNOWLEDGMENT

The author is indebted to F. S. Malm, W. G. Straitiff and H. J. Peters of these laboratories for assistance in connection with this work.

ADDENDUM

After this paper was submitted for publication, a new sample of balata latex was received from Dutch Guiana through the agency of Hermann Weber Co., New York City. This latex, received in a tightly stoppered glass bottle about one month after tapping, was clean and milky white and had about the same viscosity as normal rubber latex. Some fermentation had set in and the *p*H value on receipt was found to be 4.2. A particle size and analysis made by F. F. Lucas showed the maximum, minimum and average sizes to be 3.9, 0.13 and 0.80 microns, respectively. This new latex analyzed as follows:

	Per cent
Total solids	43.6
Resin on solids	44.6
Water-soluble matter and dirt in solids	12.0
Balata hydrocarbon in solids by difference	43.4
Ratio gutta/resin	0.97
Nitrogen in solids	0.40
Ash in solids	0.69

The resin resembled that of the "white" latex previously investigated. The above analysis indicates that this latex differs from the "white" latex either because of differing location of the tree from which it was tapped or because of seasonal variations. The differences noted are not basic and could be the result of variations in tree type or of climatic and soil differences.

REFERENCES

[1] The botanical classification of the *Mimusops* is not complete as was indicated by a recent summary of the situation by Chevalier, "The Genuine and False Balata Trees", *Rev. botan. appl. agr. trop.*, V, 12 Bull. No. 128, April **1932**, p. 261-282; 347-358. In the Guianas there appear to be at least two *Mimusops* varieties which are tapped in the preparation of commercial sheet balata. These have been described botanically as the *Mimusops* balata, Gaertn. and the *Mimusops Surinamensis*, miq., both coming under the general name *Mimusopa globosa* and the common English name of bullet tree. The block balata from Venezuela also is prepared from the genuine *Mimusops* whereas, the inferior Brazilian white block balata of commerce known as *Ecclinusa* balata, Ducke, is prepared from mixed latices of several *Sapotaceae* which have not been botanically well defined.
[2] "Latex", New York: Chemical Catalog Co., **1930.**
[3] *Ind. Eng. Chem.* **30,** 146 (1938).
[4] Kemp, *Ind. Eng. Chem.* **30,** 154 (1938).
[5] *J. Soc. Chem. Ind.* **24,** 898 (1905).
[6] *Kolloid-Z.* **14,** 262 (1914).
[7] *Trop. Agr., Ceylon* **59,** 267 (1922).
[8] *Nature* **123,** 601 (1929).
[9] Ruzicka, *Ann.* **471,** 21 (1929).
[10] *J. Soc. Chem. Ind.* **23,** 529 (1904).
[11] *J. Soc. Chem. Ind.* **27,** 1123 (1908).
[12] *J. Soc. Chem. Ind., Japan* **38,** 504 (1935).
[13] A suitable method for preparing pure balata hydrocarbon is as follows: Dry balata coagulum or sheet balata is dissolved in pure chloroform. This solution is washed with water until it is clear and water-white. Acetone is added slowly to the chloroform solution until the balata hydrocarbon is precipitated. The precipitate is washed with a mixture of acetone and chloroform. The precipitate is redissolved and reprecipitated. Carbon dioxide is used to prevent oxidation and to remove the solvent in the final drying operation conducted at 50° C.
[14] "Chemistry and Technology of Rubber", Reinhold Publishing Corp. **1937,** p. 716.
[15] "Chemistry and Technology of Rubber", Reinhold Publishing Corp. **1937,** p. 561.
[16] Kautschuk **8,** 137 (1932).
[17] *Trans. Inst. Rubber Ind.* **5,** 71 (1929).
[18] Ber. **57,** 1266 (1924).
[19] *J. Res. Natl. Bur. Standards* **13,** 357 (1934).
[20] *India-Rubber J.* **90,** Intern. No. 36 (1935).
[22] U. S. Dept. Commerce Trade Promotion Series No. **41** (1927).

X-RAY DIFFRACTION PATTERNS OF CRYSTALLINE SOL RUBBER PREPARED FROM ETHEREAL SOLUTION *

GEORGE L. CLARK,[1] SIEGFRIED T. GROSS [2] and W. HAROLD SMITH

INTRODUCTION

In a previous publication[3] there was reproduced an x-ray diffraction pattern of crystals obtained from a solution, cooled to temperatures between −40° and −50° C., of an ether-gel fraction of rubber from *Hevea brasiliensis*. Measurements of three strong interferences indicated that the crystals were similar to those of stretched gel rubber and of frozen sol, gel and total rubber. Although many attempts were made at that time, unsatisfactory diffraction patterns were obtained with crystalline ether-sol rubber. The interferences were faint and not suitable for accurate measurement and analysis. Since the crystalline material is bulky and some specimens are more compact than others, it seemed possible that the average number of cell diameters was too small to permit sharp definition, and that more material was required for the examination by x-rays. However, it is not certain that lack of definition was caused by insufficient crystalline rubber. The possibility that parts of the long-chain molecules become crystalline and that parts remain amorphous is not excluded, and might be its cause. Additional work with crystalline sol rubber, using a slightly different experimental procedure and more material than in earlier experiments, finally resulted in a satisfactory pattern.

PREPARATION OF THE SPECIMENS

The crystalline sol rubber, prepared as has been previously described[4], was collected by filtration in a paper thimble having a smooth inner surface free from detachable fibers. During filtration, a cold current from solid carbon dioxide was impinged on the opening of the thimble. To remove amorphous rubber, the crystalline material was thoroughly washed with successive portions of ethyl ether, which were chilled to temperatures below −35° C. to avoid dissolving the crystals. The ether was finally displaced by 95 per cent ethyl alcohol which had been previously cooled to −10° C., and the thimble was transferred to a glass container filled with cold alcohol. The container, packed in solid carbon dioxide, was shipped to the University of Illinois for examination by x-rays.

X-RAY MEASUREMENTS

For the present investigation the collimating tube of the low-temperature cylindrical camera of Wolthuis[3] was lengthened and, as a result, patterns could be made at a distance of approximately 2.6 cm. The exact distance from the specimen to the film was determined by calibration with sodium chloride. The specimen holder was cooled by the exhaust from solid carbon dioxide.

* Reprinted from the *Journal of Research of the National Bureau of Standards*, Vol. 22, No. 1, pages 105-107, January 1939. Research Paper Rp 1170.

TABLE I

X-RAY DIFFRACTION RESULTS

R	*θ*	*d*
Crystallized sol rubber—Distance from specimen to film, 2.57 cm.		
cm.	Degrees	A
0.65	7° 6′	6.21
.82	8° 51′	5.00
1.01	10° 44′	4.14
1.14	11° 57′	3.71
Crystallized gel rubber—Distance from specimen to film, 10.32 cm.		
2.62	7° 7.5′	6.19
3.31	8° 53.5′	4.97
4.04	10° 41.5′	4.14
"Frozen" sol rubber—Distance from specimen to film, 10.32 cm.		
2.63	7° 9′	6.18
3.32	8° 55′	4.96
3.61β	9° 38′	4.15
4.59	11° 59′	3.70

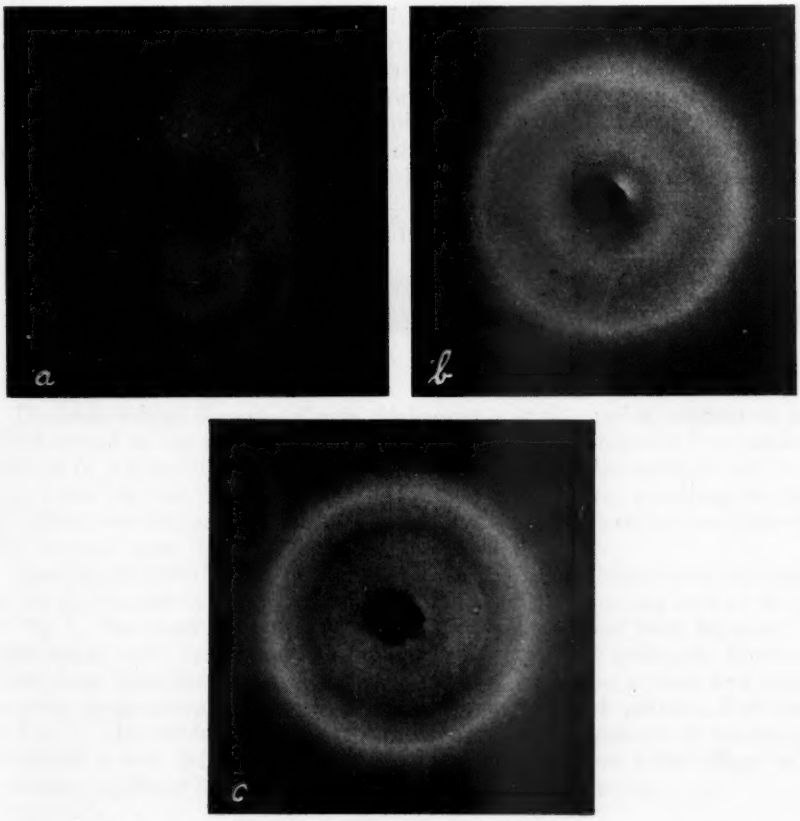

FIG. 1.

Typical x-ray patterns which have been obtained are shown in Figure 1(a, b and c). They represent successive attempts to procure well defined interferences. A double halo is present in Figure 1(a). This pattern was produced by unfiltered $K\alpha$ radiation from copper, and it is entirely different from that of gel rubber and of unstretched total rubber. The spacings corresponding to the two rings differ completely from the one fundamental halo which is characteristic of unstretched total rubber. The pattern could be interpreted as that of a liquid crystal rather than of a three-dimensional solid. The melting of some of the crystals during the transfer of the sample to the cooled camera could be assigned as its origin, even though the opaque crystalline rubber, stable below approximately 0° C., had not become noticeably transparent, as is usual when the crystals melt completely. The pattern with the double halo was obtained with three samples of the same lot of crystalline sol rubber, and at first was thought to have a special significance. However, there had been evidence of faint but definite interferences in other samples, and observations of crystalline rubber between crossed nicol prisms indicated that the pattern of a truly crystalline material should be obtained.

Patterns shown in Figure 1(a and b) were obtained with unfiltered $K\alpha$ radiation from copper during an exposure of 3 hours. In Figure 1(b), partial resolution of the double halo has taken place, and in Figure 1(c) it has proceeded to definite interferences, which were measured. The results in Table 1 were obtained with four lines, and for comparison, interplanar distances of similar lines from crystallized gel rubber and from frozen rubber are reproduced. Frozen gel and frozen total rubber gave similar values which are not included. In the Table, d is the distance between the set of planes making an angle θ with the incident beam, and R is the radius of the diffraction ring as measured on a flat film.

L. G. Polhamus, Bureau of Plant Industry, Department of Agriculture, supplied the *Hevea* latex used in this work, and his kindness is acknowledged.

REFERENCES

[1] Professor at the University of Illinois.
[2] Special Research Appointee, University of Illinois.
[3] Clark, Wolthuis and Smith, *J. Research Natl. Bur. Standards* **19**, 479 (1937).
[4] Smith, Saylor and Wing, *Bur. Standards J. Research* **10**, 479 (1933).

EXAMINATION OF THIN RUBBER FILMS BY ELECTRON DIFFRACTION *

KENZO TANAKA

It was reported in a preceding paper (*Mem. Coll. Sci. Kyoto Imp. Univ.* [A] **21**, 85(1938)) that when a thin film of certain organic long-chain molecules coating a polished metal surface is heated, the regular arrangement of the molecules of the substance becomes haphazard at a temperature which is characteristic of the substance and differs from its melting point. This temperature was called the transition temperature of the molecular arrangement of the substance. In the present experiments the manner of the arrangement of the rubber molecules in a thin film deposited from benzene solution on a polished metal surface was examined in the same manner as before.

FIG. 1.

To obtain rubber films of different thicknesses, a small piece of polished copper which served as the backing of the film was dipped for a moment in a benzene solution of rubber. The range of rubber concentration of the solution was from 2 to 0.005 per cent. By subsequent evaporation of benzene, a uniform coating of rubber was obtained, which was so thin as to show the interference fringe by light in most cases.

The typical diffraction patterns obtained by an electron beam which impinged on the rubber film in a direction almost parallel to its surface are such as shown in Fig. 1. But these are rare cases, and generally the rubber films deposited as above stated gave rise at first to diffuse halos of amorphous structure. However, when these amorphous films were heated at about 70° C. for a while and cooled to room temperature, they gave rise to the same diffraction patterns illustrated in Fig. 1. The regular pattern showing the regular arrangement of the rubber molecules is well defined for very thin films, and becomes more diffuse with increasing thickness of the film, as in the case of other substances.

* Reprinted from the *Memoirs of the College of Science*, Kyoto Imperial University, Series A, Vol. 21, No. 5, pages 169-172, September 1938.

The regular diffraction pattern, as shown in the illustration, is explained as being due to a certain regular arrangement of long-chain molecules standing perpendicular to the flat surface of the backing. The spacing calculated from the separations of the parallel layer lines which are nearly straight in the figure was 2.58 Å. This spacing is the same as the distance between alternate carbon atoms in the zigzag structure of a long-chain molecule. The value of the inner potential, estimated from the positions of the layer lines, was less than one volt.

From the distances of the spots on the layer lines in the diffraction pattern, as measured from the intersection of the plane of incidence of the electron beam with the photographic plate, the lateral spacings of the regular arrangement of the long-chain molecules can be calculated. The spacings thus obtained are shown in the third column of Table I. In column 1 and 2 of the table the indices and the spacings of the planes parallel to the *c*-axis of the crystal of paraffin found by Müller are given. The agreement between the values in column 2 and in column 3 shows that the lateral disposition of the molecules of rubber in

TABLE I

1	2	3	4	5	6
Paraffin		Rubber			
Indices	Spacings A	Reflect.	Transm.	Paraffin Transm.	Al-foil Transm.
100	7.45	—	—	—	—
010	4.97	4.94	—	—	—
110	4.13	4.07	4.07	4.12	4.15
200	3.72	3.69	3.69	3.77	3.72
210	2.98	2.98	—	—	2.94
020	2.48	2.50	2.47	2.47	2.47
120	2.37	2.37	—	—	—
220	2.07	2.11	—	2.075	2.04
400	1.86	1.79	—	—	—
410	1.74	1.66	—	—	—
420	1.49	1.47	—	—	—
040	1.24	—	—	—	—
140	1.23	1.23	—	—	—
240	1.18	1.11	—	—	—

the present case is the same as that of a paraffin crystal. This arrangement of the molecules of rubber differs from that found in stretched rubber by means of x-rays.

The agreement between the structures of rubber and paraffin was also tested by transmission photographs. A rubber solution in benzene and a paraffin solution in benzene were spread as thin films on thin foils of aluminum which had been carefully cleaned. After the evaporation of the solvents, diffraction photographs were taken by sending an electron beam normal to the surface of the films. The results are shown in columns 4 and 5 of Table I. Again the agreement is evident. Aluminum foils usually give rise to certain extra rings due to some fatty substances in the transmission photographs, such as shown in column 6 of Table I. These extra rings can be removed by carefully washing the foil, and in the examination of rubber and paraffin described above such cleaned foils were always used.

Next to see whether the regular diffraction pattern obtained with rubber may be due to other fatty substances present in the rubber film as impurities, diffraction photographs were taken with the backing only and with the backing which was dried after being covered thickly with benzene and volatile oil. The benzene

and volatile oil were the same as those used as the solvent of rubber and in cleaning the backing. But in these cases no such regular diffraction pattern as shown in Fig. 1 appeared, even when the specimens were heated to about 90° C. Next, the surface of the rubber film which had given rise to the regular diffraction pattern as in Fig. 1 was cleaned with volatile oil to remove any fatty substances which might be present on the surface of the rubber film as a contamination. But no appreciable change in the diffraction pattern was observed with such specimen before and after the cleaning.

As a result of these tests, the suspicion that the regular diffraction pattern observed with a thin film of rubber deposited on a smooth surface of a metal might be caused by fatty substances present in the film as impurities seems to be almost removed; consequently the view that rubber molecules arrange themselves in the same manner as paraffin in the present case seems to be almost certain.

When the thin rubber film in which the rubber molecules were arranged regularly, as has been described, was heated in the vacuum of the electron diffraction apparatus, no appreciable change in the regular diffraction pattern was observed at temperatures below about 60° C., but with rise of temperature above this the pattern became diffuse and finally vanished at about 66° C. Such a transition temperature, at which the regular arrangement of the molecules becomes haphazard, was measured in the same way with ten specimens of different thicknesses. The transition temperature thus measured ranged from 58° C. to 66° C., and no regular relation was found between the transition temperature and the thickness of film. This transition of the molecular arrangement of rubber from regular to irregular is reversible and, when a heated specimen is cooled, the molecules arrange themselves regularly, as before, nearly at the transition temperature.

The writer wishes to express his sincere thanks to Prof. U. Yoshida for his invaluable suggestions.

EXTERNAL INFLUENCE AND THE INTERNAL STATE OF RUBBER *

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INTRODUCTION

With continued progress in technology, highly elastic products have come to be of great importance at the present time. Whereas in earlier years rubber was the only product which could be classed in this category, in the last few years many new products with properties resembling those of rubber have been added to the list. This is to a great extent due to the fact that chemical research has given a better insight into the parent substance of rubber and the structural nature of rubber itself. According to these researches, rubber is representative of a group of highly polymeric, organic natural substances, whose long molecules are composed of small structural units in uninterrupted repetition.

By reproducing artificially the relations existing in the structure of the rubber molecule, it has been possible by chemical synthesis to prepare highly elastic substances from allied substances or from substances which polymerize in an analogous way. But in spite of this success, chemical investigations have not yet reached a point where it is possible to explain the mechanism of elasticity, for actually elastic phenomena do not depend on chemical changes; an explanation is rather to be sought in changes which take place in the relative positions and forms of the rubber molecules.

To explain the phenomena on this basis, it is necessary to make further studies of the freedom of motion and actual movements of the molecules and the active forces involved. The solution of this problem can be attacked from two different directions, in one case by experimentation, in the other case by theory as the chief weapon.

From the experimental point of view, the problem is first to demonstrate directly, by external effects, the movements of molecules, and then to follow the progress and nature of these movements. From the theoretical point of view, which has been the method of attack followed particularly by Meyer and his collaborators[1], Kuhn[2], Mark and Guth[3], the possibilities have been worked out which, on the assumption of chain molecules, involve the simplest form, position and movement of the rubber molecules.

The first step in an experimental treatment of this problem is to follow the changes in state and the effect of external influences on the occurrence and cessation of these changes. In this case the effects of these changes in state are not necessarily identical with the cause of elasticity, for the changes represent the final stages of the phenomena resulting from stressed conditions in rubber, which in turn account for its elastic behavior. In view of this, one would expect it to be possible to come to some conclusion as to the part played by the molecules themselves in elastic phenomena by a consideration of the behavior of the molecules during changes in state.

To do this, it is first of all necessary to study more closely the appearance and progress of the changes in state.

* Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 15, No. 1, pages 11-14, January 1939.

DETECTION OF CHANGES IN STATE AND THE FOLLOWING OF THESE CHANGES

The changes in state which rubber undergoes can be demonstrated in various ways, *e.g.*, by x-ray diagrams, by double refraction, by changes in density, by changes in light absorption and by changes in mechanical properties. It should be pointed out, however, that the utility of any one of these methods is limited, and for this reason the use of more than one method in studying a substance is advisable, for by using several methods and properly interpreting the results it is possible to eliminate all errors which result from variability of the sample. From this point of view, examination by x-rays and by polarized light can be used with advantage to supplement one another. These methods were adopted in the experiments to be described.

X-RAY EXAMINATION OF THE FORM OF RUBBER UNDER DIFFERENT CONDITIONS

The x-ray diagram of rubber at ordinary temperatures and not under mechanical stress shows a broad faint ring or halo, *i.e.*, the diagram of an amorphous substance. On the contrary, the x-ray diagram of rubber stretched to

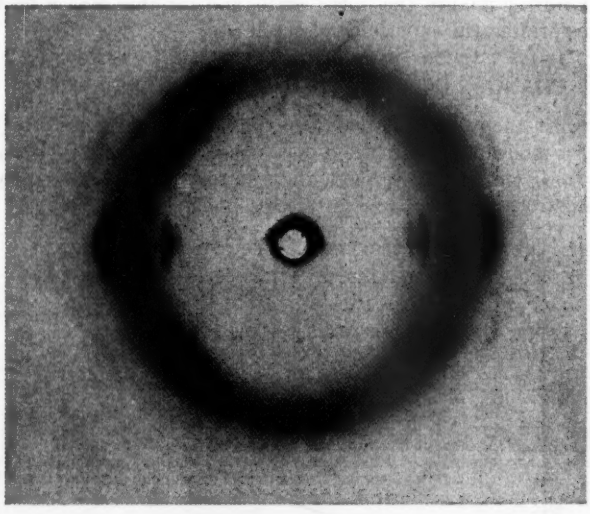

FIG. 1.—X-Ray diagram of a vulcanized rubber thread stretched approximately 320 per cent (FeK radiation; chamber diameter 114.4 mm.).

a considerable degree shows sharp interference points. The appearance of these points proves that the rubber molecules have become oriented in a lattice-like arrangement, and further that the newly formed lattice is oriented in the direction of stretching. This phenomenon was discovered by Katz[4] and investigated more thoroughly by Meyer and Mark[5], von Susich[6], Sauter[7], Hauser and Rosbaud[8], Acken, Singer and Davey[9] and others.

Figure 1 is a reproduction of an x-ray diagram of a vulcanized rubber thread stretched to about 320 per cent elongation. The intensities of the faint halos and

the intensity of the interference points make it possible to draw conclusions as to the relative quantities of ordered and unordered molecules of the substance.

The first indications of a lattice-like arrangement in unvulcanized rubber at ordinary temperatures appear at an elongation of about 70 per cent; in vulcanized rubber at 250 to 300 per cent elongation. Although the lattice-like orientation is not to be attributed solely to stretching, the latter does not accelerate the orientation, for in the x-ray diagram of frozen rubber (brought about by prolonged storage at 5-10° C.) sharp Debye-Scherrer lines appear. These are of course an indication of the formation of lattices, even though these lattices are distributed in an unordered arrangement. The agreement of the two lattices shows that crystallization takes place in both cases. This conclusion is verified by the fact that such a change in state is accompanied by an increase in density and evolution of heat. In this connection the investigations of Hock[10], Feuchter[11], Kirchhof[12] and van Rossem[13] are particularly worthy of attention.

The identity in the position and gradation in intensity of the x-ray interference points shown by vulcanized and unvulcanized rubber indicates that each has the same lattice. If this is so, it should be possible to ascribe, with certain limitations, the phenomena observed in vulcanized rubber to unvulcanized rubber.

In the new investigations to be described, vulcanized rubber was chosen as a subject of study, because the plastic flow phenomena which take place in unvulcanized rubber modify the initial state, and for this reason lead to complications in interpreting the experimental results.

CHANGES IN STATE AND DOUBLE REFRACTION

Although with the x-ray method it is possible to gain an insight into the arrangement of molecules, the method does not aid in explaining the initial states of crystallization. On the other hand, these latter can be followed by measuring the optical anistropy, *i.e.*, the double refraction.

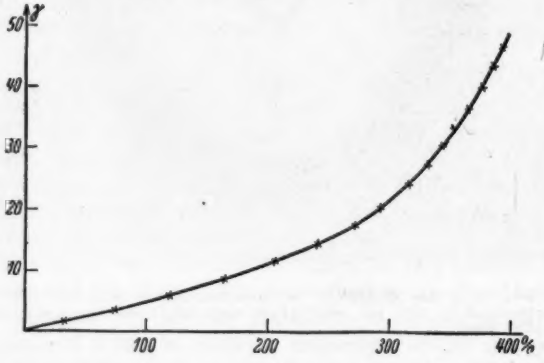

FIG. 2.—Double refraction as a function of the degree of elongation. Elongation approximately in 8.53 minutes. The abscissa represents elongation as percentage of the original length; the ordinate represents double refraction in sodium-light units, calculated to 1 mm. thickness in all cases. Temperature 20° C.

In the unstretched state rubber is an isotropic substance, but even a slight elongation brings about a measurable state of anisotropy[14].

Figure 2 shows measurements of the double refraction as rubber is stretched continuously. Here the double refraction increases steadily, and within the range

of 250 to 300 per cent elongation there is a notable increase in the slope of the curve.

Parallel experiments with x-rays indicated that in the lower part of the curve there is no lattice-like orientation. The double refraction which was observed is merely a double refraction caused by the stress; only in the range beyond 300 per cent elongation did the crystallized phase appear.

Although the double refraction caused by stress is attributable to a straightening of the molecules, the true double refraction of the crystallites then enters into the phenomena, as a result of which the total double refraction increases and thereby causes the notable increase in slope of the curve.

CHANGES IN STATE AS A FUNCTION OF TIME

Based on facts known at the present time, it appears that the process of molecular arrangement comes to an end as soon as the rubber is stretched no farther or very soon thereafter. If so, after the rubber is stretched no farther,

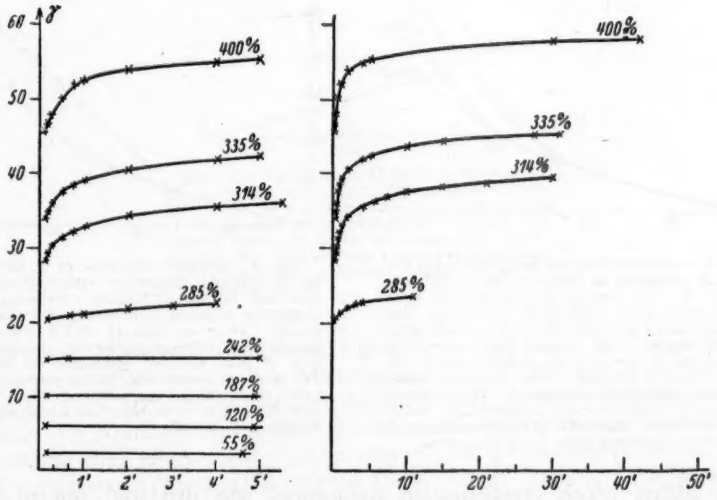

FIG. 3.—Spontaneous changes in double refraction with time after rapid stretching, measured at various degrees of extension. The abscissae represent time (in minutes). The ordinates represent double refraction in sodium-light units calculated to 1 mm. thickness. The parameter is the degree of extension. Temperature 20° C.

the double refraction would necessarily assume a definite value which would then remain constant. Actually this is not always the case.

Figure 3 shows the double refraction, as a function of time, at various degrees of elongation, when the rubber was stretched rapidly and then held stretched at the various elongations. Whereas the double refraction remained constant after the rubber was stretched to relatively low degrees of elongation, it increased spontaneously in cases where the rubber had been stretched beyond a certain definite precentage elongation. This increase was great enough to be measurable over a long period of time.

x-Ray diagrams of these samples showed that the double refraction increases only after the molecules have arranged themselves in lattice formation. This phenomenon corresponds to a process of crystallization, and it is evident in x-ray

diagrams as an increase in the intensity of the interference points. This observation is in accord with the observations of Acken, Singer and Davey[15], who found that a certain interval of time is necessary for an x-ray diagram to develop.

As a matter of fact, crystallization is a phenomenon which requires time for the molecules to arrange themselves from the crystallizing liquid into their positions in the lattice.

A further confirmation of this is to be had in the density measurements of Holt and McPherson[16]. These authors showed that the density of a vulcanized rubber thread increased appreciably for a long time after the rubber was stretched no farther.

Figure 4 is a summary of the individual measurements obtained at various temperatures. The curves represent measurements 10 seconds, 1 minute and 5 minutes after suspension of the stretching. As the temperature increased, the

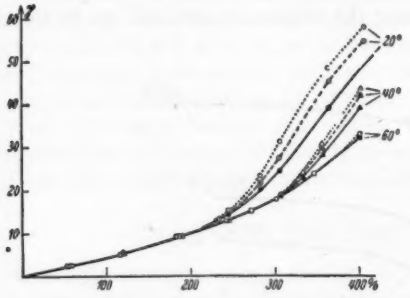

FIG. 4.—Double refraction as a function of the degree of extension at temperatures of 20°, 40° and 60° C. The curves are constructed from measurements made with rapid stretching. The solid-line curves give the values 10 seconds after rapid extension; the broken-line curves the values after 1 minute; the dotted curves the values after 5 minutes. The abscissa represents the percentage elongation; the ordinate the double refraction in sodium-light units, based on 1 mm. thickness. The parameters are temperature and time after rapid extension.

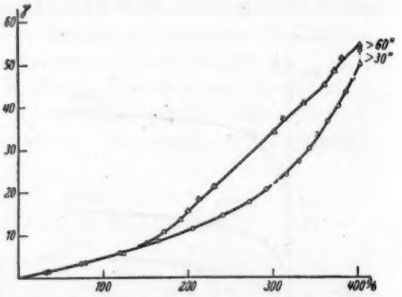

FIG. 5.—Double refraction as a function of the percentage elongation with uniform extension and release of tension (hysteresis). The elongation required 8.53 minutes (circles on diagram). After an interval of 1.5 minutes, the sample was released uniformly through a period of 9.83 minutes (triangles on diagram). The abscissa represents the percentage elongation; the ordinate represents double refraction in sodium-light units based on 1 mm. thickness. Temperature 20° C.

range within which crystallization commenced was displaced toward higher degrees of elongation, as was confirmed by x-ray diagrams. This result is in accord with the fusion curve of natural rubber plotted from x-ray data by von Susich[17].

The tendency of the double refraction to approach a final constant value at a diminishing rate might lead one to assume that there is in rubber an equilibrium between the crystalline phase and the amorphous fused substance, the state of which is governed by the degree of elongation and by the temperature. This phenomenon would then be strictly analogous to the dependence of the melting point on the pressure. The influence of pressure from all directions on crystallization has been shown by Thiessen and Kirsch[18], whose work proves that an increase of pressure on all sides of a sample of unvulcanized rubber increases the temperature of crystallization. On this basis, it is not the elongation which should be regarded as the effective agent in bringing about crystallization, but rather the pressure which is exerted on the system. The influence of pressure on crystallization was suspected by Wöhlisch[19] by analogy from his observations on the transformations of collagen.

CHANGES IN STATE AND HYSTERESIS PHENOMENA

Although we are not yet in a position to construct an accurate equilibrium curve of the relation between the crystallized substance and amorphous liquid substance, it is possible at least to indicate the range within which this equilibrium must lie. This range is indicated by the hysteresis curve. Such a curve, represented in Figure 5, was obtained by taking measurements while rubber was stretched uniformly and released after short periods of rest.

As the x-ray diagram shows, the crystalline phase appears throughout the recovery curve, and it disappears only where this curve joins and coincides with the original extension curve. That this hysteresis phenomenon is related to the presence of a crystalline phase is indicated by the curve shown in Figure 6; this curve is a section below the range of elongation within which the crystalline phase is formed. Similar hysteresis phenomena appear in changes in density and changes in mechanical properties.

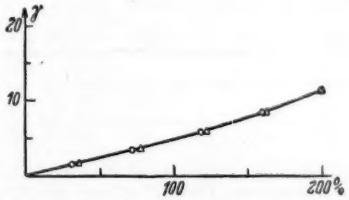

FIG. 6.—Double refraction as a function of the percentage elongation, with uniform stretching to 200 per cent elongation and uniform rate of release after an interval of 1.5 minutes. Extension shown as circles on the graph; release as triangles. The abscissa represents percentage elongation; the ordinate double refraction. Temperature 20° C.

The various hysteresis phenomena which have just been discussed cannot be explained satisfactorily by flow phenomena. Rather they are to be ascribed to changes in the state of rubber and therefore they depend on the crystalline component, for although during flow the molecules slide past one another into new positions, they retain during the process of flow a "heredity effect" of their original arrangement, since after release from tension there is no appreciable residual elongation.

THE INFLUENCE OF TEMPERATURE ON THE INTERNAL STATE

The influence of temperature on the internal state of rubber was studied in more detail by following the changes in melting point. Figure 7 shows the various measurements. The ordinate represents double refraction, the abscissa represents time. After stretching at 20°, a short time interval was allowed. An increase in temperature brought about an immediate decrease in the double refraction, which however showed no further change when the temperature remained constant. On cooling, the rubber thread crystallized again and the double refraction increased.

A thread stretched 210 per cent, in which no crystalline phase was present, showed no dependence on temperature, as may be seen in Figure 7.

In a parallel series of experiments (see Figure 8) x-ray diagrams confirmed the results of the double refraction measurements. It was found first of all that the

dependence of double refraction at any particular elongation on temperature is attributable to the crystalline component.

The trend of the double refraction-melting point curve shows that, with increase in temperature, fusion takes place progressively. This is particularly evident from

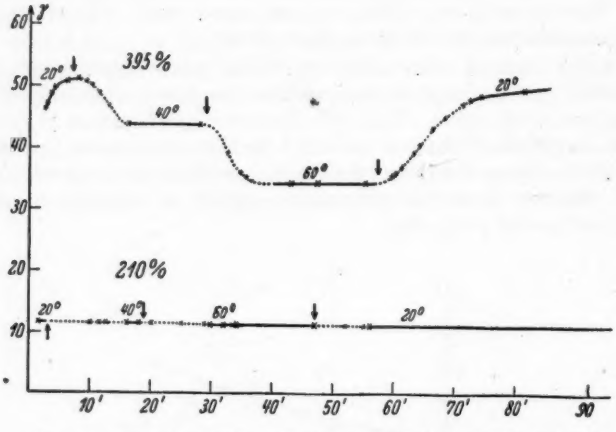

FIG. 7.—Changes in double refraction after rapid elongation and subsequent heating and cooling. The solid parts of the curves represent measurements at constant temperature; the arrows show the times at which heating or cooling commenced. The dotted parts of the curves represent measurements while the temperature was changing. The abscissa represents the time in minutes; the ordinate the double refraction in sodium-light units, calculated to 1 mm. thickness. The parameters are percentage elongation and temperature.

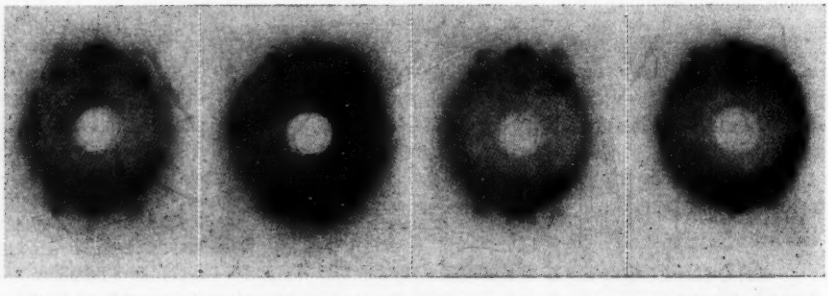

FIG. 8.—Influence of changes in temperature on the x-ray diagram of a vulcanized rubber thread elongated 400 per cent. These diagrams were obtained at 20°, 60°, 20° and 40° C, with CuK radiation, chamber diameter 57.2 mm., time of irradiation 30 minutes. The roentgenographs were prepared under like conditions.

the x-ray diagrams, which were obtained from a rubber thread stretched 400 per cent. The series of diagrams correspond in this case to the chronological order in which they were taken. Heating from 20° to 60° C., with subsequent cooling to 20° C., led to continuous and at the same time reversible fusion. The x-ray diagram taken at 40° C., which is also included, is in harmony with the other facts.

According to all this, rubber in a stretched condition does not have a definite, invariable melting point but only a wide fusion range.

RÉSUMÉ

The observations recorded in the present paper show that the changes in state which rubber undergoes depend on a series of factors. These factors include not only mechanical influences but also to a particularly great extent temperature and time.

Although investigations up to the present time give a certain insight into these phenomena, a large number of new experiments may ultimately be necessary to explain in a conclusive way the mechanism of the changes in state.

These changes in state are by no means of mere scientific interest; they are of considerable importance from a technical point of view in that they may be reflected in the particular properties of rubber which play so important a part in its processing and in the characteristics of the finished product.

REFERENCES

[1] Meyer, von Susich and Valkó, *Kolloid-Z.* **59**, 208 (1932); Meyer and Ferri, *Helv. chim. acta* **18**, 570 (1935), *Kautschuk* **11**, 92 (1935).
[2] Kuhn, *Kolloid-Z.* **68**, 2 (1934); **76**, 258 (1936); *Z. angew. Chem.* **37**, 640 (1938).
[3] Mark and Guth, *Naturwissenschaften* **25**, 353 (1937); *Z. angew. Chem.* **36**, 205 (1937).
[4] Katz, *Naturwissenschaften* **13**, 411 (1925).
[5] Meyer and Mark, "Der Aufbau der Hochpolymeren Organischen Naturstoffe", Leipzig **1930**, 203.
[6] von Susich, *Naturwissenschaften* **18**, 915 (1930).
[7] Sauter, *Z. physik. Chem.* **36B**, 405 (1937).
[8] Hauser and Rosbaud, *Kautschuk* **3**, 228 (1927).
[9] Acken, Singer and Davey, *Ind. Eng. Chem.* **24**, 54 (1932).
[10] Hock in Memmler's "Handbuch der Kautschukwissenschaft", Leipzig **1930**, 436.
[11] Feuchter, *Kautschuk* **2**, 262 (1926).
[12] Kirchhof, *Kautschuk* **2**, 155 (1926).
[13] van Rossem and Lotichius, *Kautschuk* **5**, 2 (1929).
[14] von Bjerkén, *Ann. Physik* **43**, 808, 818 (1891), Rossi, *Beibl. Ann. Physik* **35**, 206, 264 (1911); **36**, 67 (1912); Kröger, *Kolloid-Z.* **45**, 46 (1928); Zocher, *Kautschuk* **8**, 173 (1929); Geel and Eymers, *Z. physik. Chem.* **3**, 240 (1929).
[15] Acken, Singer and Davey, *Ind. Eng. Chem.* **24**, 54 (1932).
[16] Holt and McPherson, *J. Res. Natl. Bur. Standards* **17**, 657 (1936).
[17] von Susich, *Naturwissenschaften* **18**, 915 (1930).
[18] Thiessen and Kirsch, *Naturwissenschaften* **26**, 387 (1939).
[19] Wöhlisch and du Mesnil du Rochemond, *Z. Biologie* **85**, 406 (1927); *Naturwissenschaften* **26**, 380 (1938).

INHIBITION OF CRYSTALLIZATION OF RUBBER BY HIGH PRESSURE *

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Bekkedahl[1] has shown that crude rubber at atmospheric pressure freezes in the temperature range from $-40°$ to $+10°$ C. and melts in the temperature range from 6° to 16° C. The transition is from amorphous rubber to crystalline rubber which is the stable modification between $-72°$ and 6° C. His measurements of the freezing at 0° C. showed that about 280 hours were necessary for completion of the transition, the volume decreasing by 2.2 per cent in such a manner that the volume-time curve was S-shaped.

This communication reports the inhibition of crystallization at high pressure. Crude smoked sheets were packed tightly in a pressure chamber and isopropyl alcohol was used to transmit the pressure. The chamber was kept at 0° C. in a well-circulated ice bath. A pressure of 8000 kg. per sq. cm. was applied, and its constancy observed over a period of 14 days. The sensitivity of the manganin gauge used for pressure measurement was such that changes of 5 kg. per sq. cm. were detectable. Outside of slight erratic pressure changes caused by change of temperature around part of the press that was not kept at 0°, "no change of pressure due to crystallization was detected during the 14 days." Examination of the rubber immediately after pressure was released showed that it was still in the amorphous state.

Since the specific volume of amorphous rubber is greater than that of crystalline rubber, pressure raises the transition point, and it can be said that the inhibition is due to supercooling. Using the data of Bekkedahl[1] and Bekkedahl and Matheson[2] for melting temperature, change of specific volume on melting and heat of fusion, computation by Clapeyron's equation shows that the melting point of crystalline rubber is of the order of 400° C. at 8000 kg. per sq. cm. The inhibition of crystallization appears to be an effect of high viscosity of amorphous rubber at high pressure. Extremely high viscosities have been observed[3] in complicated organic compounds under pressure, and when it is considered that the molecular aggregates in crude rubber may number several hundred chemical molecules, it is to be expected that the viscosity of amorphous rubber at 8000 kg. per sq. cm. may be increased enormously. Staudinger has computed an average molecular weight of a raw rubber in the hundred thousands, a value indicating that the pressure coefficient of viscosity must be very high, since it is known that this coefficient increases with molecular weight.

The transition from crystalline rubber to amorphous rubber at high pressure appears to be an equilibrium phenomenon, however. Samples of smoked sheet crystallized at atmospheric pressure were observed to melt at 77.5° C. at a pressure of 1270 kg. per sq. cm. dT_m/dp is then 0.0484 as compared with a calculated value of 0.0518° C./kg. per sq. cm. by Clapeyron's equation at atmospheric pressure on the assumption that the normal transition point is 16° C. Melting took place slowly, approximately five minutes being required for completion. If the normal melting point of the rubber is taken at 11° rather than 16° C., the above value for melting under pressure will be increased accordingly.

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Because of high viscosity it would appear that amorphous rubber can be kept in the metastable state over a long period of time at 8000 kg. per sq. cm. Bekkedahl concluded that the rate of crystallization of rubber below −50° C. at atmospheric pressure was too small to be measured during several weeks of observation. Examples of delayed equilibrium are well known. Deville observed a transition in sulfur over a period of 2 years, and it has been observed that the transition from white to gray tin at 18° C. may require several centuries for completion under ordinary conditions. Many polymorphic changes at high pressures have been found by Tammann, Bridgman and Cohen to take place very slowly, although the transitions are quite different in nature from the one discussed here.

The writer is indebted to Lawrence Wood of the National Bureau of Standards for suggesting these experiments and contributing much helpful advice.

REFERENCES

[1] Bekkedahl, *Nat. Bur. Standards J. Research* **13**, 411 (1934).
[2] Bekkedahl and Matheson, *Nat. Bur. Standards J. Research* **15**, 512 (1935).
[3] Dow, Morgan and Fenske, *Ind. Eng. Chem.* **29**, 1078 (1937).

A FEW CORRECTIONS OF STATISTICAL THEORIES OF THE HIGH ELASTICITY OF RUBBER *

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1. INTRODUCTION

Theories have of late been developed to account for the high elasticity of certain substances, particularly rubber, over a particular range of elongation. These theories are based on the assumption that the molecules have taken a spherical form, which is the one statistically most probable. We wish to prove that, in order to avoid wrong conclusions, certain modifications in these theories are necessary, and we wish especially to make a stand against the following two assertions:

(1) That rubber-like high elasticity is always associated with the presence of chain molecules.

(2) That when rubber is elongated, no attractive forces are broken down and no valence angles are deformed until an elongation of about 350% is reached.

2. HIGH ELASTICITY AND THE CHAIN-LIKE FORM OF MOLECULES

The opinion is often expressed in the literature[1] that the presence of long flexible chains is an essential condition for rubber-like high elasticity[2]. We would therefore point out that there are today known structures which have high elastic qualities, but which without doubt have three-dimensional molecules. For instance, there are the phenol-formaldehyde resins in the so-called B stage, which under suitable conditions can be stretched elastically to an extent of 240% and more[3]. Under roughly the same conditions it can be easily observed that shellac possesses an elastic deformability of approximately 180%[4]. Finally, we would draw attention to substances like vulcanized rubber, polymerized Neoprene and polymerized linseed oil, whose original chain structures have been transformed into three-dimensional ones by cross-linking[5] and whose high-elastic qualities are well known. A few years ago[4] some general postulates were put forward for the occurrence of high elasticity, the most important are as follow.

High elasticity can be observed when strong bonds occur next to much weaker ones, and when constituent parts with bonds of great energy are of considerable dimensions, for instance, of high molecular weight. We believe that this hypothesis still includes the right conditions for high elasticity. The restriction to the presence of chain molecules is in any case too narrow.

Another question is whether the high elasticity of substances with a three-dimensional structure obeys the statistical laws to which we shall revert later. In our opinion it may be possible, as long as the cross-linking has not exceeded a certain extent, that equation (5) and the conclusions that can be drawn from it will apply. This idea has already been advanced in connection with rubber by Kuhn[6], who considers the formation of sulfur bridges during vulcanization a favorable factor in preventing the so-called macro-Brownian movement of thread-like molecules. In this connection it should be pointed out that so far all experiments[7] have been made with lightly vulcanized rubber.

* Reprinted from the *Mededeelingen van de Rubber Stichting*, Amsterdam, No. 11, pages 5-12, February 1939.

3. THE PART PLAYED BY ATTRACTIVE FORCES IN THE ELONGATION OF RUBBER

The statistical views first advanced by Wöhlisch[8] and by Meyer[9] and later developed by Meyer's own school[7] and also by Mark[10], Kuhn[6] and Guth[11] in particular, are mainly based on the following experimental results. An increase was observed in the tension of rubber, *elongated to a certain extent (to approximately 350%)*, as the temperature was raised[7], namely:

$$\sigma = cT \quad \ldots\ldots (1)$$

σ = tension, c = constant, T = abs. temperature.

From this one can draw the very important conclusion[6, 7] that in the case of isothermal elongation of rubber:

$$\left(\frac{dU}{dl}\right)_T = 0, \quad \ldots\ldots (2)$$

$$\left(\frac{dA}{dl}\right)_T = -T\left(\frac{ds}{dl}\right)_T \quad \ldots\ldots (3)$$

U being internal energy, A external work, l length and s entropy.

This shows that *there is no increase in internal energy during isothermal elongation and that the applied energy only effects a decrease in entropy.*

Proceeding from this standpoint, Meyer[7] concluded that in contrast with metals and similar substances there is no change in the potential energy of rubber during isothermal elongation. It would therefore appear that no attractive forces are broken down and no valence angles are deformed.

It is especially these conclusions regarding the non-neutralization of attractive forces that we wish to dispute below. Our objections are mainly based on the fact that, contrary to the supposition of Kuhn[12], one cannot take for granted that the C–C bonds of rubber chains possess unlimited power of free rotation. In connection herewith attention must be drawn, for example, to Mack's model[13] of the rubber molecule, which is represented in Fig. 1.

The fundamental difference between this model and others frequently referred to elsewhere is that a very different volume is allotted to the H atoms, which fact affects, above all, the power of rotation (Fig. 1). Thus, there can be free rotation only about the axes marked (1) and (3). In this way an elongation of the molecules by 300 to 400% can be attributed solely to rotation[14].

We must note especially that Mack, taking the heat of evaporation of normal hexane (C_6H_{14}) as a basis, calculates the work of detachment of a gram-atom of hydrogen from a hydrocarbon surface to be 500 calories. As a result of the rotation mentioned above, three H–H points of contact are detached during elongation and the potential energy of the system [$(dU_1/dl)_T$ in equation (4)] would increase by 1500 calories for each gram-molecule of isoprene (68 grams).

If this model of Mack's is adopted, there is at once apparent a second cause of the storing up of internal energy [$(dU_2/dl)_T$ in equation (4)], *i.e., the distortion of the valence angles,* owing to the fact that there is not unlimited freedom of rotation in this model. It is too early to make a quantitative statement about this with safety: Meyer and Ferri (*loc. cit.*) have already pointed out this effect, but considered it relatively insignificant.

There is a third possibility of the storing up of internal energy during elongation, but in a negative sense, *i.e.,* the increase in the number of H–H contacts between adjacent molecules. It is an effect which has already been designated

condensation by Mack and which we shall indicate in formula (4) by $(dU_3/dl)_T$. In addition to this[15] there is the possibility of *crystallization* when the orientated and partially condensed molecules are snapping in to the crystal lattice $[(dU_4/dl)_T$ in formula (4)]. In this way 10 calories per gram of rubber are gained. In the terminology of Kuhn[16] one might say that the micro-Brownian movement does not cease at condensation but only when crystallization occurs. The relative increase in surface as the molecules unwind will promote both condensation and crystallization.

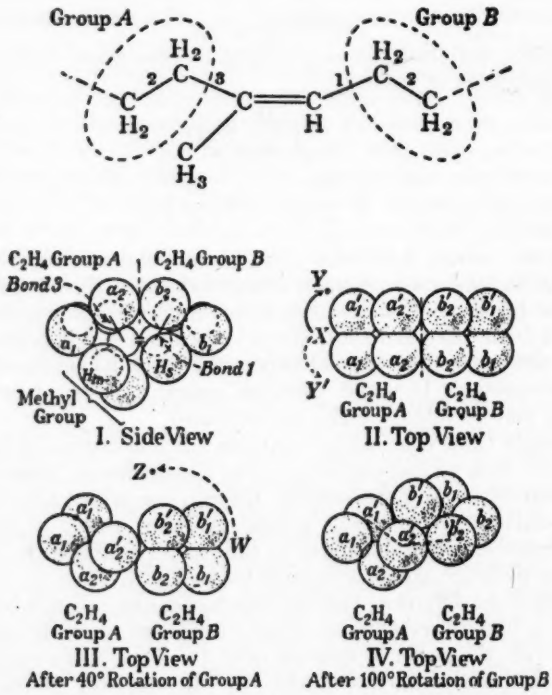

FIG. 1.—Structural formulas of the extension of rubber (according to Mack). C_2H_4 group *A* rotates 40° on bond 3. C_2H_4 group *B* rotates 100° on bond 1. Group *A* functions as a group *B* for the next pair of doubly bonded C atoms.

It is a question of primary importance whether these condensation and crystallization effects play a part during elongation up to 350%; Meyer and Kuhn reject the possibility, mainly on the results of x-ray examination[17].

On the other hand, in our opinion x-ray photographs do not show enough detail to be decisive on these questions. In the x-ray diagram of a substance with irregularly distributed crystallites, the rings are distinct only if the diameter of the crystallites is between 10^5 and 10^2 Å[18]. If the particles are smaller than 10^2 Å, the lines are already broadening. In this connection it is particularly interesting to note that at an elongation of no more than 100% Trillat was able, by means of electron diffraction, to obtain distinct point diagrams, proving the existence of a regular arrangement of orientated molecules[19]. The lattice showed the periods 8.1 Å (fibre axis) and 12.4 Å, which coincide with the crystal periods determined

at greater elongations with the aid of x-rays. It was further demonstrated that these regular intervals did not exist in the undeformed material.

It is therefore probable that certain chains form already minute crystallites $[(dU_4/dl)_T$ in equation (4)], for instance twofold or threefold, which perhaps only touch at odd points, while the x-ray diagram would still indicate an entirely amorphous structure.

Summarizing, we may say that according to Mack's molecular model—which in our opinion is roughly correct—four different possibilities of changes in the internal (potential) energy due to isothermal elongation can be substantiated. The task is now to prove the consistency between this conclusion and the results of experiments showing that there is no change in internal energy [equation (2)].

We proceed from the supposition that the changes in the internal energy U_1, U_2, etc. already mentioned, really occur.

For the sake of simplicity we shall also assume that in the case of rubber only four dU/dl terms exist, although there are possibly still more. Griffith[20], for instance, assumes a rotation energy of the chain as a whole. It is possible that in the case of substances other than rubber the limitation introduced will likewise not always apply.

For the isothermal elongation of rubber we therefore write:

$$\Sigma\left(\frac{dU}{dl}\right)_T = \left(\frac{dU_1}{dl}\right)_T + \left(\frac{dU_2}{dl}\right)_T + \left(\frac{dU_3}{dl}\right)_T + \left(\frac{dU_4}{dl}\right)_T \quad \ldots\ldots\ldots (4)$$

increase of the potential energy as a result of rotation; increase of the potential energy as a result of distortion of valence angles; decrease of the potential energy as a result of condensation; decrease of the potential energy as a result of crystallization

The experiments[21] mentioned show in cases of elongation of 0−350%:

$$\left(\frac{dU_1}{dl}\right)_T + \left(\frac{dU_2}{dl}\right)_T = -\left(\frac{dU_3}{dl}\right)_T - \left(\frac{dU_4}{dl}\right)_T \quad \ldots\ldots\ldots (5)$$

and in cases of elongation to the extent of more than 350%:

$$\left(\frac{dU_1}{dl}\right)_T + \left(\frac{dU_2}{dl}\right)_T < -\left(\frac{dU_3}{dl}\right)_T - \left(\frac{dU_4}{dl}\right)_T \quad \ldots\ldots\ldots (6)$$

We may therefore say that lightly vulcanized rubber is a substance which is characterized by the fact that in case of elongation of 0−350% and at temperatures of from −60° to about +80° C. equation (5) happens to apply, while in case of greater elongation equation (6) applies.

The question may now be asked why, for a certain elongation, the positive $(dU/dl)_T$ effects exactly compensate the negative ones. In reply to this question we would point out that the condensation and crystallization effects dU_3 and dU_4 of an elongated isoprene group can occur, according to the theory of Mack, only if the group has previously been unwound.

Every dU_1 value of 1500 calories per molecule accordingly will correspond to a certain negative (dU_3+dU_4), when dU_2 is neglected (see above). For each unwound isoprene group 1500 calories will be liberated therefore. In order to explain the increasing values of $\left(\frac{dU_3}{dl}\right)_T = \left(\frac{dU_4}{dl}\right)_T$ in equation (6) in case of elongation above 350%, it should be borne in mind that when practically all the isoprene groups are unwound and the chains, in consequence of the increasing elongation, contact with each other more closely, the possibilities of crystallization are particularly great.

The foregoing theories make it comprehensible that during elongation up to 350% the volume remains constant; it may be said in the first approximation that (dV/dl) will be nearly equal to (dU/dl) and as long as $\Sigma\ (dU/dl)=0$ this may also be expected approximately of $\Sigma\ (dV/dl)$.

In view of the fact that an elongation of more than 350% causes a decrease of the internal energy, Meyer and Ferri[22] particularly emphasize the fact that under such circumstances also attractive forces cannot play a part, *as the internal (potential) energy would otherwise necessarily increase.* In the foregoing we have already put forward our objections to this assertion on the ground that attractive forces can very well be released during elongation (dU_1); the decrease in energy (dU_4) however, as a result of the intensive crystallization which now sets up, exceeds the sum of the energy increases.

For other highly polymerized substances the conditions under which equations (5) and (6) apply will vary according to the values U_1, U_2, U_3, U_4 and perhaps also U_5 etc. In the case of polyvinyl acetate, for instance, the validity conditions for (5) would appear to begin at about 200% and 50° C.[23], of cellulose and derivatives[24] it is questionable whether the conditions for (5) exist at all.

In conclusion let it be stressed that the energy changes dU_1, dU_2, etc., *may on no account be looked upon as causes of the elastic recovery of rubber.* The contracting tension is a consequence of the lowered entropy, otherwise the value of (U_1+U_2) would be greater than the values of (U_3+U_4) in (5) and (6).

We have elaborated our theories merely to secure a clear idea of the molecular model and of the changes it undergoes during elongation, this being hardly possible without correct insight into the energy factors involved.

SYNOPSIS

The writer proves that high elasticity occurs not only in compounds with chain-like molecules, but also in substances consisting of three-dimensional molecules.

Meyer and his collaborators demonstrated that in the case of isothermal elongation the internal energy of the rubber remains constant up to an elongation of 350%. Starting from the model suggested by Mack, the writer makes it appear probable that this observation may have to be interpreted otherwise than has been done hitherto. It is suggested, that with such elongation the resultant positive and negative changes in internal energy compensate one another. Only above an elongation of about 350% do the effects of condensation and crystallization (dU_3+dU_4) predominate over the effects of detachment and valence deformation (dU_1+dU_2).

This conclusion is contrary to the opinion of Meyer that attractive forces play no part in case of elongation, but is of great importance for obtaining a better insight into molecular changes during the elongation of highly polymerized substances.

REFERENCES

[1] Meyer, von Susich and Valkó, *Kolloid-Z.* **59**, 208 (1932); Mark, *Nature* **141**, 670 (1938).
[2] By high elasticity is meant elastic deformability > 1%; cf. literature quoted under Note 5.
[3] Houwink, *Trans. Faraday Soc.* **32** (1936); cf. also Note 5.
[4] Houwink, *Kolloid-Z.* **77**, 183 (1936).
[5] For a summary see Houwink, "Plasticity and Structure of Matter", Cambridge 1937.
[6] Kuhn, *Kolloid-Z.* **76**, 258 (1936); *Z. angew. Chem.* (1938) in the press.
[7] Meyer and Ferri, *Helv. chim. Acta* **18**, 570 (1935). For later extensive experiments see Hauk and Neumann, *Z. physik. Chem.* (A) **182**, 285 (1938).
[8] Wöhlisch, *Verh. physik.-med. Ges. Würzburg* (N. F.) **51**, 53 (1926).
[9] Meyer and collaborators, *Kolloid-Z.* **59**, 208 (1932).
[10] Mark, *loc. cit.*

[11] Guth and Mark, *Monatsh.* **65**, 93 (1934).
[12] Kuhn, *loc. cit.*
[13] Mack, *J. Am. Chem. Soc.* **56**, 2757 (1934). A summary is given on pages 216-219 of the book quoted in Note 5.
[14] This idea apparently applies to organic substances in general because here the hydrogen-carbon bond has a homopolar character, the hydrogen atom having an extra negative electron in common with carbon. For similar models see Stuart, *Physik. Z.* **35**, 990 (1934).
[15] We owe this clear distinction to a conversation with J. Hoekstra.
[16] Kuhn, *loc. cit.*
[17] Meyer and Ferri, *loc. cit.*; Hauk and Neumann, *loc. cit.*
[18] Dehlinger, *Z. Metallkunde* **23**, 147 (1931). Brill, *Erg. techn. Röntgenkunde* **2**, 115 (1931).
[19] Trillat, *Kolloid-Z.* **69**, 384 (1934).
[20] Griffith, Can. *J. Research* **10**, 486 (1936); cf. Note 5.
[21] Meyer and Ferri, *loc. cit.*; Hauk and Neumann, *loc. cit.*
[22] Meyer and Ferri, *loc. cit.*
[23] Misch and Picken, *Z. physik Chem.* (B) **36**, 398 (1937).
[24] Meyer and Lotmar, *Helv. chim. Acta* **19**, 68 (1936).

HEAT OF DILUTION IN THE SYSTEM: RUBBER-TOLUENE *

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It is already known that the heat of dilution of a system can be derived from the temperature coefficient of the osmotic pressure. This method is an example of the indirect method supplementing direct calorimetric measurements which have been carried to a high degree of perfection by Swietoslawski. The present brief work is dedicated to this master of calorimetric research.

It may be in keeping with the present work first of all to review the theoretical principles of the indirect method. The equation relating heat content to the temperature coefficient of free energy can be expressed thus[1]:

$$\left[\frac{\partial\left(\frac{F}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_P = H$$

For one component (1) of a solution, this equation becomes:

$$\left(\frac{\partial\left(\frac{\overline{F}_1}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P = \overline{H}_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $\overline{F}_1 = \left(\frac{\partial F}{\partial n_1}\right)_{n_2}$ and $\overline{H}_1 = \left(\frac{\partial H}{\partial n_1}\right)_{n_2}$

are the partial free energy and the partial heat content, respectively, referred to a gram-molecule.

On the other hand, the derivative of the free energy with respect to pressure is equal to the partial molecular volume:

$$\left(\frac{\partial \overline{F}_1}{\partial P}\right)_T = \overline{v}_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The osmotic equilibrium is represented by the condition:

$$F_{1(P)} = F_{1(P^0)}{}^0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where P is the pressure on the solution and P^0 is the pressure on the solvent (component 1).

From Equation (2) is obtained, by integration, the equation:

$$\overline{F}_{1(P)} - \overline{F}_{1(P^0)} = \int_{P^0}^{P} \overline{v}_1 \, dp \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

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* Translated for Rubber Chemistry and Technology from Przemysl Chemiczny, Vol. 22, No. 11-12, pages 441-443, November-December 1938.

By introducing the condition of osmotic equilibrium (Equation 3), the following relations are derived:

$$F_{1(P^0)}{}^0 - F'_{(P^0)} = -(\overline{F}_1 - \overline{F}_1{}^0)_{P^0}$$
$$= \int_{P^0}^{P} \overline{v}_1 \, dp \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Then by applying Equation (1), *i.e.*, by dividing Equation (5) by the temperature T and the derivative with respect to $1/T$, the following relation is obtained:

$$\left[\frac{\partial\left(\frac{\overline{F}_1 - F_1{}^0}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right] = \left[\frac{\partial\left(\frac{\int_{P^0}^{P} \overline{v}_1 \, dp}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right] = \overline{H}_1 - H_1{}^0 \quad \ldots\ldots\ldots (6)$$

From a practical point of view, it is satisfactory merely to measure the osmotic pressure at two temperatures T and T'; in this case the following relation is employed:

$$H_1 - H_1{}^0 = \frac{\frac{\left[\int_{P^0}^{P} \overline{v}_1 \, dp\right]_T}{T} - \frac{\left[\int_{P^0}^{P} \overline{v}_1 \, dP\right]_{T'}}{T_1}}{\frac{1}{T} - \frac{1}{T'}} \quad \ldots\ldots\ldots\ldots\ldots (7)$$

In order to calculate any results from this relation, it is necessary to know v_1, which in the present case is the partial molecular volume of toluene, as a function of the pressure, composition and temperature.

Changes in $\overline{v}_1$, with pressure may be disregarded, for they are smaller than 0.001 when the pressure is less than 4 atmospheres[2]. Moreover, as has been verified by the present authors in measurements of the density of rubber solutions, the partial molecular volume of toluene for concentrations of rubber lying between 0 and 5 per cent is equal to the molecular volume $\overline{v}_1{}^0$ of pure toluene.

It then is possible to derive the following relation:

$$\overline{H}_1 - H_1{}^0 = \frac{\frac{[\overline{v}_1{}^0(P - P^0)]_T}{T} - \frac{[\overline{v}_1(P - P^0)]_{T'}}{T'}}{\frac{1}{T} - \frac{1}{T'}} \quad \ldots\ldots\ldots\ldots\ldots (8)$$

where $P - P^0$ is the osmotic pressure.

The changes in the molecular volume of toluene with changes in temperature are considerable, *i.e.*, they are of the same order of magnitude as the changes in osmotic pressure. They are shown in Table I, which gives the results of measurements at two different temperatures.

TABLE I

t	T	$1/T$	d_1	$v_1 = M_1/d_1$
24.4	297.4	3.36×10^{-3}	0.8590	107.3
35.6	308.6	3.24×10^{-3}	0.8493	108.6

where $M_1 = 92.6$

The raw material studied was masticated rubber, approximately 95 per cent of which was soluble in toluene. The undissolved portion was separated by centrifuging, which gave a homogeneous solution. This solution, containing 2.52 per cent by weight ($w=0.0252$), had at 19.4° C. a relative viscosity of 27 with respect to toluene.

The cell described by Herzog[3] and illustrated[4] in Figure 1 was adopted for the work. Membrane M pressed against a brass screen P and was held between two brass blocks E (75×15×75 mm.), each hollowed out in such a way as to form a double cylindrical cell 50 mm. in diameter. Each half-cell communicated on the one hand with a capillary tube, and on the other hand with a filling tube

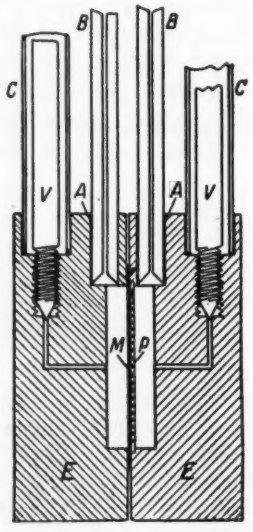

FIG. 1.

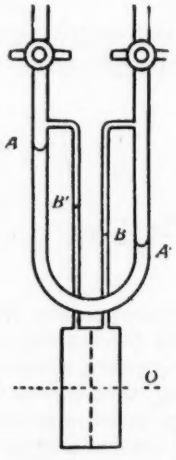

FIG. 2.

provided with a needle-valve seal. The glass tubes were joined to the brass by Wood alloy. The membrane consisted of an Ultra-Cella Filter of the Physikalische Werkstätten A.-G. of Göttingen. The compensation method of van Campen was employed. The arrangement of the capillaries and the manometric tubes serving for compensation[5] are represented in Figure 2.

The entire apparatus was placed in an air thermostat. The differences in level in the tubes were measured from the outside by means of a cathetometer. The difference in pressure between the two chambers could, under these conditions, be expressed (in mm. of water at 4° C.) thus:

$$P=(B-O)d_s-(B'-O)d_t+(A-A')d_m$$

where d_s, d_t and d_m are the densities of the solution, toluene and manometric liquid, respectively. The meaning of the other letters is evident in Figure 2.

In making such measurements, the first operation is to apply a higher pressure on the solution than that on the solvent. If it is found, by examination of the levels B and B′ in the capillary tubes, that toluene is passing from the solution through the membrane to the pure solvent, the difference in pressure between the two chambers is greater than the osmotic pressure. This difference in pres-

sure is then reduced so that toluene passes in the opposite direction. The osmotic pressure then lies between these two pressures. By reducing progressively this interval, it is possible to measure, in a single day, the osmotic pressure with a precision better than ±0.3 per cent.

After making the first measurement, the thermostat is adjusted to a higher temperature. Equilibrium is reached in one night, after which a new measurement is made. By repeating this set of measurements for several days, changing

TABLE II

No.	w grams of rubber (per gram of solution)	t	$P-P^0$ (mm. of water)	π (atmospheres)	$\pi v_1/T$ (cc.-atm./ degree)	$H_1-H_1^0$ (calories)
1	0.0470	24.4	515	4.99×10^{-2}	$+2.7 \times 10^{-4}$	$+5.5 \times 10^{-2}$ ($\pm 1 \times 10^{-2}$)
		35.6	536.5	5.19×10^{-2}		
2	0.0352	24.4	301.5	2.92×10^{-2}	$+1.3 \times 10^{-4}$	$+2.6 \times 10^{-2}$ ($\pm 1 \times 10^{-2}$)
		35.6	313	3.03×10^{-2}		
3	0.0203	24.4	107.5	1.04×10^{-2}		
4	0.0065	24.4	14.6	0.14×10^{-2}		

alternately from one temperature to the other, the osmotic pressure as a function of time at the two temperatures is obtained. Extrapolation to zero time can then be made.

The curves representing the osmotic pressure as a function of time for concentrations of 4.70% and 3.52% of rubber (No. 1 and No. 2) are reproduced graphically in Figure 3. Each measurement is represented by the two limiting pressures within which the osmotic pressure lies. Zero time is when the osmotic

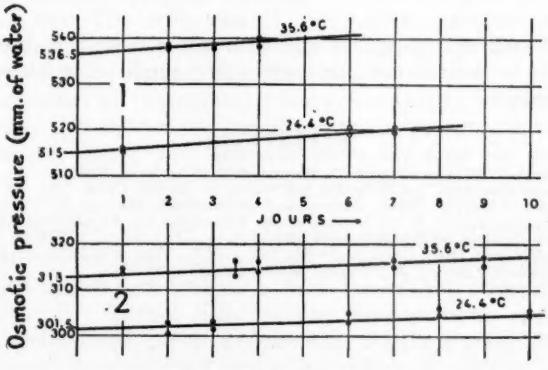

FIG. 3.

cell is filled. It would have been possible to choose the time when the rubber had gone into solution, but this would have made only an insignificant difference in the results. Table II gives the extrapolated values of the osmotic pressures, and also the heats of dilution calculated by means of Equation 8. Measurements 3 and 4 were carried out at the same temperature, for in this range of concentrations, the precision is not great enough to evaluate the heat of dilution.

It will be seen that $\overline{H}_1-H_1^0$ is positive, *i. e.*, addition of one gram-molecule of toluene to a large volume of solution is accompanied by an absorption of heat.

This result is of interest in that it is evidence that the large deviation of the system: rubber-toluene, from the ideal solution cannot be explained by an energetic interaction between rubber and toluene (solvation).

When the π/w values are plotted as a function of w, a straight line is obtained (Figure 4). In extrapolating to the composition: $w=0$, the law of Raoult can be

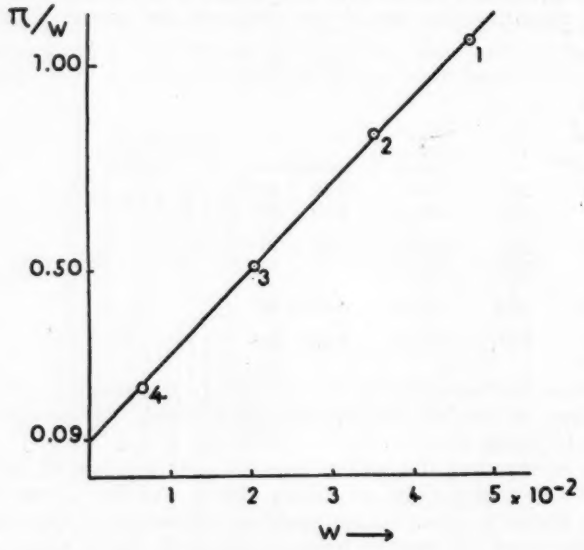

FIG. 4.

applied. If the molecular weight of toluene is taken as 92, a molecular weight of $230{,}000 \pm 30{,}000$ is derived for the particular sample of rubber used in the present experiments.

REFERENCES

[1] See Lewis and Randall, "Thermodynamics", McGraw-Hill, New York, **1923.**
[2] For a more detailed discussion, see Boissonas and Meyer, *Z. physik. Chem.* [B], **40**, 108 (1938).
[3] Herzog and Spurlin, *Z. physik. Chem., Bodenstein-Festband* **1931**, 239.
[4] Reproduced with authorization of the Editors of the *Zeitschrift für Physikalische Chemie,* whom we take pleasure in thanking for their kindness.
[5] See Boissonas and Meyer, *Helv. Chim. Acta* **20**, 783 (1937). The permission of *Helvetica Chimica Acta* to reproduce Figure 2 is gratefully acknowledged.

STRENGTH OF VULCANIZED RUBBER *

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For many years the determination of tensile strength has been regarded as one of the operations of major importance in the physical testing of vulcanized rubber. In more recent years the evaluation of tear strength has been recognized as almost equally important, and it is perhaps natural that attempts should have been made to correlate the two quantities.

Tear tests involve the use of transverse cuts or nicks and a non-uniform stress concentrated at the base of the cut. Most tear tests are empirical, the figures obtained depending on the shape and dimensions of the test-piece, a matter on which there is no general agreement. Little is known concerning the mechanism of tearing.

Accidental imperfections in the cut edges of tensile test-pieces have been considered as the main cause of variations within a group of duplicate test results. This view has been contested by other workers, who maintain that these are chance variations depending on a number of factors. It is nevertheless generally agreed that a nick or similar imperfection in the edge of a tensile test-piece profoundly alters the distribution of stress so that the force required to rupture becomes less, but no adequate theory has yet been propounded to explain quantitatively how this occurs.

The normal tearing of textile fabrics, etc., is usually carried out by applying a pull at right angles to the cut, whereas paper is frequently torn by holding down one side of the cut and applying a pull to the other at a smaller angle to the direction of the cut. The main part of the problem therefore is the effect of transverse cuts in a test-piece subjected to a straight pull. The further question of the effect of the angle of the pull may be considered later.

The limiting values of the applied force are obviously of great importance, being respectively the true tensile strength when the specimen is completely free from imperfections, and a tear strength when the cuts are producing their maximum effect. As characteristics of the material, intermediate values are of little worth except in special cases.

Preliminary Experiments.—If a rectangular specimen of thin rubber sheet bearing a cut at right angles to one long edge be clamped close to the cut (Fig.1A) and the free end loaded with weights, a small lateral displacement of the center line occurs (Fig. 1B). Thus a truly vertical pull cannot be applied by direct loading, and a symmetrical specimen is essential. Simple experiments showed that the lowest force was required when the cut was simple, no material being removed. A specimen shaped as in Fig. 1C required a force almost as large as that required by a tensile test-piece and a specimen shaped as in Fig. 1D ruptured when only a small force was applied. Hence it may be concluded that the cause of the reduction is to be found in the "free" rectangular portion adjacent to the cut or even in the triangle shown in Fig. 1D.

Specimens used in subsequent work therefore were rectangular and carried two opposed cuts (Fig. 1E) so that the center line was not displaced. They were

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 14, No. 4, pages 242-264, December 1938.

extended until ruptured in a standard Scott tensile testing machine. Thus the test resembled an ordinary tensile test. During the test the cut opened to a shape which often appeared to be part of a circle (Fig. 1F).

The Effect of Dimensions.—In all cases the specimens were cut by hand and were of a length sufficient to eliminate effects due to the grips. The thickness was as nearly as possible 1 mm., and each result was corrected in the usual manner for small variations from the standard thickness.

In the following description d is the width of the center (uncut) strip in millimeters, n is the depth of the transverse cut or width of the "free" strip in millimeters and P is the load in grams per unit area of center strip and based on the original dimensions.

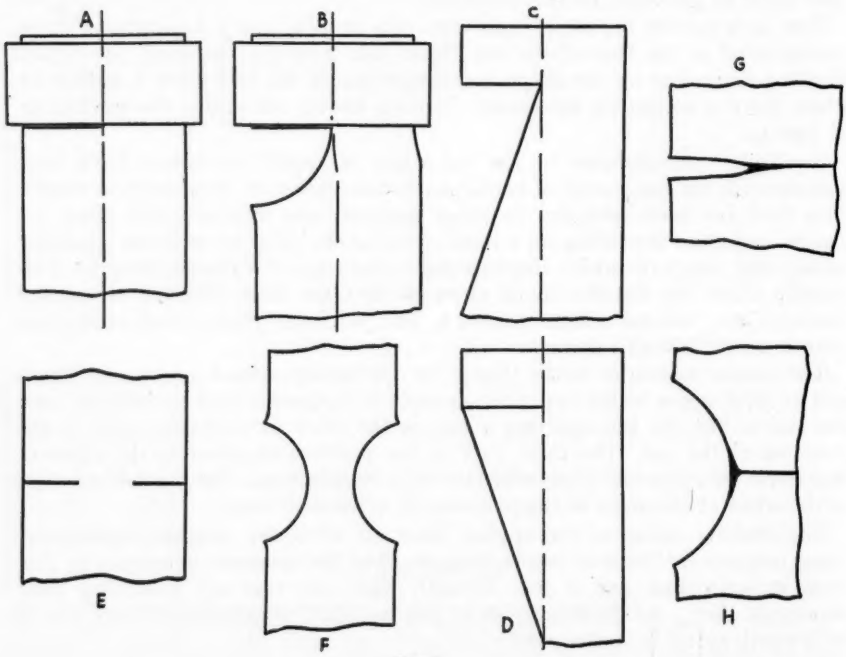

FIG. 1.

Tests showed that for a given rubber sheet if d is constant, P varied with n as as shown in Fig. 2, and if n is constant, P varied with d in a similar manner. The force decreases to a minimum and nearly constant value when the center strip is wide and the nick is deep. These conditions are also those of least sensitiveness to accidental variations of dimensions.

These curves appear to be hyperbolic in form, one asymptote being the vertical axis and the other being a line parallel to but not usually coincident with the horizontal axis. They fit the equation:

$$P-p=kn^m$$

where p, k and m are constants for the particular rubber stock used. p represents the position of the horizontal asymptote, *i.e.*, the theoretical minimum load to rupture by means of a straight pull and this may be considered as a tear resistance. When *log* $(P-p)$ is plotted against *log* n a straight line is obtained.

It may be pointed out that in the experiments of Busse (*Ind. Eng. Chem.*, **26**, 1194 (1934)) the *total* width of the specimen was kept constant and his load curve therefore rose again when the cut was very deep and the center portion was narrow.

Experiments showed that for many stocks a sufficiently large value of d was 10 mm. and attention may therefore be concentrated on the curve dealing with variation of load with n when d is constant at 10 mm.

Examination of Various Stocks.—A number of stocks was prepared, containing various fillers and various accelerators and each was sheeted to 1 mm. thick,

TABLE I

COMPOSITION OF STOCKS

Stock No.	Main components per 100 vols. of rubber
1	42 vols. gas black.
2	17 " zinc oxide.
3	45 " talc.
4	40 " whiting.
5	9 " light magnesium carbonate.
6	17 " clay.
7	45 " factice.
8	135 " lithopone.
9	10 " zinc oxide.
10	10 " light magnesium carbonate.
11	10 " clay.
12	Pure.

TABLE II

Stock No.	p g. per sq. mm.	k g. per sq. mm.	m	Modulus (g. per sq. mm.) at 30%	100%	400%	TSB per sq. mm.	EB %
Paper	2000	1265	0.24	very high				
3	258	83	0.62	112	287	1100	1040	400
8	224	63	0.33	380	—	—	444	36
4	40	80	0.85	85	190	850	1700	505
5	110	63	1.10	60	137	520	2220	640
6	91	69	1.24	50	111	500	1630	600
7	58	32	0.60	42	112	310	830	615
1	150	1600	0.60	128	255	1725	2680	540
2	146	300	1.52	58	130	645	2530	610
9	140	320	1.80	61	140	810	3040	600
10	119	120	1.45	74	188	1270	3640	605
12	97	1250	2.80	46	99	340	2930	660
11	89	100	1.35	63	151	960	3360	605

well shrunk, and vulcanized in the press to a technical cure. The standard dumbbells used for tensile tests were cut across the grain, as also were the rectangular strips, so that tearing would proceed along the grain. All tests were performed on a Scott tensile machine at standard speed, using 6 specimens for each test and reading the maximum load. The arithmetic mean of the 6 readings was taken as the required figure.

Some of the curves obtained are shown in Fig. 3. The curves may intersect, and obviously misleading comparisons would result from the use of cuts of constant and insufficient depth. These curves were converted into straight lines by plotting $log\ (P-p)$ against $log\ n$ and the constants evaluated. In Table 2 are given the values of these constants and, for comparison, the tensile characteristics of the stocks.

The figures are divided into two groups, the former referring to stocks containing considerable loadings of inert fillers. Their strengths are in general less than 2000 grams per square millimeter and the corresponding values of the constant k are low. There is a similarity between the values of p and of k and of the modulus within this group. The curves for some of these stocks are also simple, inasmuch as the index m approximates to unity; hence the curves become straight lines when P is plotted against $\frac{1}{n}$. The second group includes the stronger stocks containing lower loadings and active ingredients. The values of k are higher and the resemblance to those of the modulus and of P is less close.

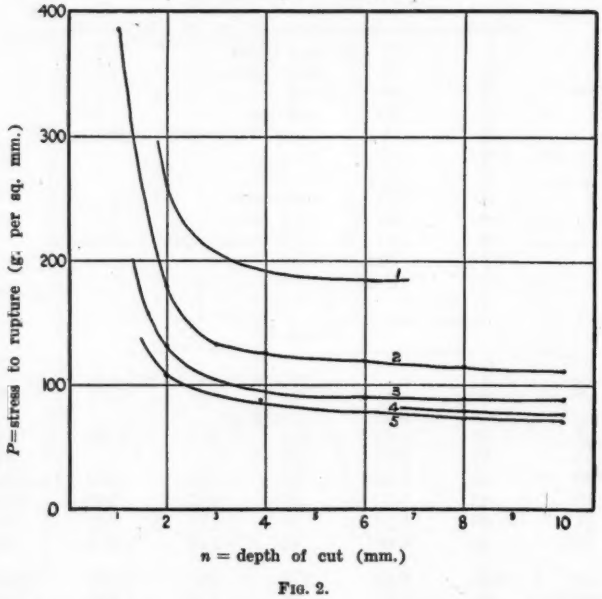

FIG. 2.

Curve 1, $d = 2$ mm.
" 2, $d = 5$ mm.
" 3, $d = 10$ mm.
Curve 4, $d = 15$ mm.
" 5, $d = 20$ mm.

Although no general relationship can be established between these figures, it can be seen that high modulus with high strength (*e.g.*, Stock 1) gives high values for p and k, and low modulus with low strength gives low values for these constants (*e.g.*, Stock 7). When the strength is not high, the higher the modulus, the greater are their values.

The Angle of Pull.—To examine the effect of applying the force at other angles to the direction of the cut, a test-piece 20 mm. wide was employed, the cut being made near one end and as far as the center line. The short end was held in a clamp, the edge of which was close to the cut (Fig. 1A) and the other end loaded directly. The clamp was mounted at the center of a graduated disc which could be rotated. Thus the pull could be applied at any angle to the cut. The results when plotted vectorially gave an ellipse. Thus a small displacement of the load from the perpendicular to the cut produces only a small change in rupturing force.

The Mechanism of Tearing.—Tearing may be described as the consecutive rupture of filaments of a material when subjected to a non-uniformly distributed stress. The tear usually proceeds from the point of maximum stress along a line approximately perpendicular to the direction of the main stress.

If an ink line be drawn joining the bases of the transverse cuts and the specimen watched carefully during the test, it can be observed that as the test proceeds the line becomes broader but also becomes widened at its ends simultaneously. The extent of this enlargement of the ends is noticeably different for different stocks, those having high modulus deforming as at G in Fig. 1 and low modulus stocks enlarging as at H.

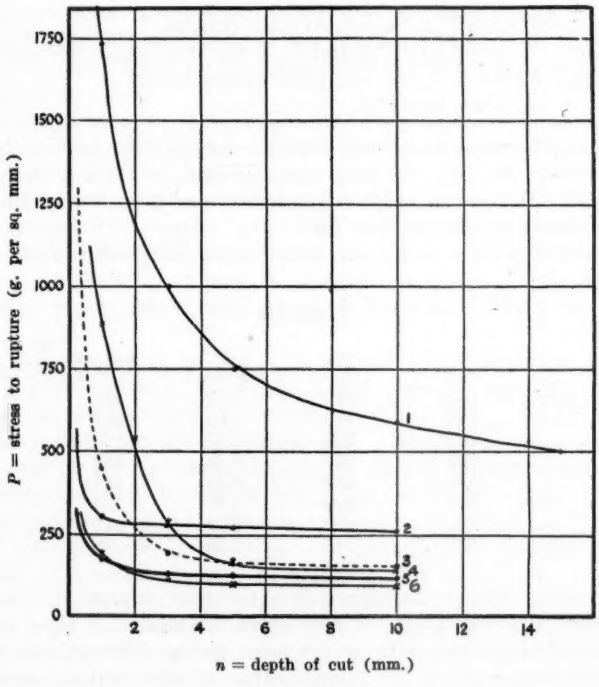

FIG. 3.

Curve 1 refers to stock 1. Curve 4 refers to stock 12.
" 2 " " 3. " 5 " " 9.
" 3 " " 2. " 6 " " 11.

It is believed therefore that tearing may be considered as having been brought about by the simultaneous action of two forces. The one is produced by the shearing action of the outer "free" strips or particularly the triangular portion of them (Fig. 1D), which produce the effect of a localized (non-uniform) extension at the edges of the center strip. The second is a general more or less uniform extension of the whole center strip as in tensile testing. The two forces are superimposed and together produce tearing.

An element of rubber at the base of the nick may be regarded as sustaining a "local" elongation E_1 and also a further elongation E_2 resulting from the general stress. The total elongation E, equal to E_1+E_2 may be assumed to be

the normal elongation at break as in tensile testing. This is probably not strictly true, but the assumption is justified in the absence of more complete information. The quantity E_2 can be measured experimentally by the use of gauge marks on the centre line of the specimen, and from the stress-strain curve the corresponding load per unit area (P_2) can be found. Hence E_1 is found and also the local stress per unit area (P_1). Now the total load to tear a specimen will be:

$$Pd = P_2 d + P_1 a$$

where a is the area which would be strained by the local stress if it were applied uniformly to produce a strain of E_1. This is referred to as the "equivalent area."

The limiting cases then are

(a) when $P_1 a = 0$, *i.e.*, no cut is present
then $Pd = P_2 d$ and P_2 is the true tensile strength
and (b) when $P_2 = 0$, *i.e.*, pure tearing occurs
then $Pd = P_1 a$.

Since P_1 cannot exceed the tensile strength and a must be less than d, then clearly Pd must be less than the total breaking load, or P must be less than the tensile strength. Any factor which tends to increase the value of the local load must operate towards a reduction of Pd.

Table 3 shows values of a for test-pieces whose dimensions were $d = 10$, and $n = 10$.

TABLE III

Stock No.	E_1 (%)	$P_1 a$ (g.)	a (sq. mm.)	Modulus (100%)	(g. per sq. mm.) at (400%)
1	450	2910	1.44	255	1725
3	368	1440	1.62	267	1100
4	480	690	0.57	190	850
5	600	470	0.38	137	520
6	570	330	0.24	111	500
2	545	630	0.47	130	645
7	480	690	0.57	112	310
12	583	145	0.08	99	340

If strips having similar dimensions but different moduli are supported as cantilevers, their free ends sag to extents which are related to their moduli. The stocks mentioned above had different densities, giving different deflecting forces, yet their deflections were in the reverse order of their moduli excepting only Stock 2 containing a high loading of zinc oxide. It was believed that the end of the ink line on the tear-specimens would be deformed in a similar manner, the sag or "local extension" increasing and the equivalent area decreasing as the modulus increased. The values of E_1 and a are compared therefore with the modulus in Table 3. The modulus at 100 per cent elongation appears to show the closer relationship.

Using one stock, the effect of increasing the depth of the cut is shown below, the value of d being constant at 10 mm.

n (mm.)	1	2	3	5
P_1 (gm. per sq. mm.)	1060	1440	1560	1660
a (sq. mm.)	0.198	0.231	0.243	0.253

Evidently as n increases so P_1 and a increase and the total tearing force decreases.

Tensile Testing.—From the hyperbolic form of the curves shown in Fig. 3 it is obvious that a very small cut causes a large fall of rupturing force. It is reasonable to suppose that the tensile strength as normally measured is really a tear strength, the tear being started by a small accidental imperfection probably at the cut edge.

This assumption is not at variance with the view that the deviations within a set of test results are due to a number of undefined influences known collectively as "chance." These chance influences also affect the results obtained with rectangular specimens as described above. Even when the dimensions are such that the test is very insensitive to accidental variations, the duplicate figures show a "spread" from the mean, of an order similar to that normally found in tensile testing. Hence it may be concluded that these chance factors do account for much of the variations, a conclusion which is in agreement with the findings of Wiegand (*Ind. Eng. Chem. Anal.*, **1**, 113 (1929)) and of Fric (*Chim. et Ind.*, April 1928, Spec. No., p. 541). Nevertheless in the above tests the effect of the cut is clearly shown.

Imperfections are known to have important effects on the strength of metals and other materials. Thus for sodium chloride, the crystal lattice theory gives the true rupture strength as 500 or more times the observed value (Zwicky, *Phys. Z.*, **24**, 131 (1923)); de Boer, *Trans. Faraday Soc.* **32**, 10 (1936)). This discrepancy has been discussed by a number of writers and is generally attributed to the presence of minute flaws. If a new surface is prepared by dissolving the old surface layer, the observed strength is increased to about ten times the normal value. Similar results have been reported for metals and other crystalline substances.

The more recent work of Griffith (*Phil. Trans. Roy. Soc.*, A**221**, 163 (1921)) on glass and particularly of Houwink (*Trans. Faraday Soc.*, **32**, 132 (1936)) and de Boer (*loc. cit.*) on synthetic resins has shown that a similar discrepancy exists in the case of amorphous substances. Houwink attributes this to the presence of gaps or voids between the macromolecules of resin (Houwink, "Elasticity, Plasticity and Structure of Matter," Cambridge University Press, **1937**).

The imperfections in tensile test-pieces of vulcanized rubber may be due to the presence of filler particles in the edge. On stretching, a particle may become detached and a potential starting point for a tear is formed. This probably explains the observation of Van Wijk (*Kautschuk*, **10**, 151 (1934)) that blunt cutters cause a smaller observed diminution of strength in loaded stocks, as in this case, the cutting imperfections would be more nearly commensurate with the size of the filler particles. On the other hand it would be expected that in pure stocks and reinforced stocks the particles would not become detached so readily and would produce smaller imperfections. In a pure stock, if complete absence of accidental flaws be assumed, the limiting value would be determined by the gaps between the rubber macromolecules. It would be of great interest if this limiting value could be determined, especially as stretched rubber shows evidence of a crystalline structure.

If the straight lines $\log (P-p)$, $\log n$ be produced until p becomes the observed tensile strength, the following values for the depth n_1 of the corresponding cut are obtained. These figures may be compared with the probable relative size of the filler particles.

It is of interest to note that the figures for the pure and reinforced stocks are impossibly large, an observation which is in line with work on glass and crystals of zinc. The reduction of strength due to cracks of given dimensions has been calculated for isotropic materials (Griffith), and comparison with experimental

results shows a large discrepancy. Cracks of 10^{-3} to 10^{-4} cm. depth for glass and even larger ones for zinc (Polanyi) are required. These results are discussed by Ewald (Ewald, Pöschl and Prandtl, "The Physics of Solids and Fluids," translated by Dougall and Deans, Blackie, **1930**, chap. 3), who points out that cracks of such dimensions would be optically visible.

It is not contended that flaws of the dimensions shown in Table 4 were actually present, but that the combination of circumstances caused the specimen to act as if such flaws were present. The other circumstances probably include slippage in the grips and accidental irregularities in placing the specimens in the grips. It may also be mentioned that the observed rupture strength of rubber decreases with increasing width of specimen, an observation which is consistent with the above results.

Further, the question of the effect of multiple nicks is raised. In tear tests of the type in question, several cuts are commonly used, as in the tear test of Ayers (Goodrich), using a crescent-shaped specimen and in the special test for belting duck described by Huxley (*Trans. Inst. Rubber Ind.* **9**, 415 (1934)). Tests on several stocks were carried out using multiple nicks 5 mm. apart and the results were identical with those obtained with the single cut. This is probably accounted for by the fact that in such tests tearing invariably occurs at one of the outer

TABLE IV

Stock No.	Filler	n_1 (mm)	Stock No.	Filler	n_1 (mm)
7	Factice	0.005	10	Light magnesium carbonate	0.13
3	Talc	0.02	2	Zinc oxide	0.20
4	Whiting	0.02	9	" "	0.38
5	Light magnesium carbonate	0.04	1	Gas Black	0.38
6	Clay	0.08	12	Nil	0.87
11	Clay	0.10			

cuts of the group. If is of interest to notice that this is also shown in Huxley's fabric test (see illustration, *loc. cit.*, p. 418).

Elimination of Cutting Imperfections—Attempts were made to remove imperfections in the cut edges of a "pure" stock by the following means:—

(*a*) by punching the dumb-bells before vulcanization in the hope that scratches would become rounded during the initial period of heating in open steam. Such specimens were compared with dumb-bells cut from open-cured sheet.

(*b*) by passing the edges of dumb-bells cut after press-cure through a flame so that the cut edges were softened locally.

(*c*) by slightly oxidizing, at room temperature, the surface of punched vulcanized specimens to form a thin film of resin.

By none of these methods was it possible to improve the observed value of the tensile strength by amounts comparable with those reported for specially prepared specimens of metals, salt, etc.

SUMMARY AND CONCLUSIONS

(1) The tearing of vulcanized rubber has been examined by the use of rectangular specimens of thin sheet carrying opposed transverse cuts and subjected to a longitudinal force. It is considered that the extreme cases are of special interest. When the cuts exert their maximum effect, a tear strength figure is obtained, and when the cuts are accidental and very small as in tensile testing, a diminution of breaking strength results.

(2) The maximum effect of the cut is experienced with wide specimens carrying deep cuts. In many cases 10 mm. width plus 10 mm. depth of cut is sufficient for practical purposes. With a constant width of the center uncut portion, the effect of increasing the depth of the cut is to cause a hyperbolic decrement of the rupture force, expressed by the equation:

$$P-p=kn^m$$

where P is the rupture force per unit area of center strip,
p is the minimum value of l when cut is very deep,
n is the depth of the cut,
k is a constant, characteristic of the material provided the center strip is wide
and m is a constant, characteristic of the material.

(3) Curves relating rupture force with depth of cut may intersect. It is therefore not possible to obtain comparisons of different materials by using a constant depth of cut unless it is large.

(4) For loaded stocks approximate relationships exist between these constants and the stress-strain functions. p, which is regarded as a tear strength, and also k diminish as the modulus decreases and m appears to increase with decreasing modulus. A number of exceptions were found however.

(5) No relationship is apparent between observed tensile strength and the values of these constants.

(6) Published work on the strength of rigid crystalline and amorphous materials has been referred to, and an attempt has been made to estimate the dimensions of the imperfections in normal tensile test-pieces of vulcanized rubber by the use of the above equation. The results show an unexpected increase as the particle size of the filler decreases, the unloaded rubber being the most imperfect. It is suggested that these figures do not represent real imperfections but that other influences predominate and cause the materials to act as if such flaws were present.

(7) Attempts have been made to obtain substantially higher tensile strength figures by special treatment aimed at removing accidental cutting imperfections, but without success.

(8) The mechanism of tearing has been discussed. Tearing is regarded as the consecutive rupture of filaments of rubber produced by the application of a non-uniform stress. In the present instance it has been shown that the total stress is composed of two portions, one of which is a "general" uniform stress. The values of p therefore do not represent the force required to produce "pure" tearing. It is concluded that the "pure" tear strength of vulcanized rubber cannot be found directly by the use of this form of test-piece.

(9) The effect of pulling at angles other than 90° to the direction of the cut has been examined. When the 90° angle is exceeded the rupture force diminishes at first slowly, then more rapidly until about 150° is reached. The rate of fall then becomes less. The results are best represented vectorially as an ellipse.

A TIME EFFECT IN THE RAPID ELONGATION OF RUBBER *

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It has already been pointed out elsewhere (Monatshefte für Chemie **72**, 32 (1938); RUBBER CHEM. TECH. **12**, 64(1939)) that the difference between the adiabatic and isothermal stress-strain curves of rubber is too great to be explained on a thermodynamic basis alone. It was suggested that the position of the adiabatic curves might be governed by the fact that the rate of stretching itself has a decisive effect on the behavior of the chains of molecules during stretching.

To throw light on this phenomenon, stress-strain curves were obtained, by means of the stretching apparatus already described in the paper mentioned, at various rates of elongation which still fell within the range of adiabatic stretching. The operation was carried out in such a way that a chronometer started electrically when the rubber began to elongate, and stopped again when the rubber reached an elongation of 450 per cent.

With the aid of this contrivance, stress-strain curves were obtained at rates corresponding to 0.68, 2.5, 5.7 and 9.1 seconds' elapsed time for the stretching. For comparison, an isotherm was obtained by loading rubber strips of the same dimensions with various weights. A vulcanizate containing 2 per cent of combined sulfur was used as experimental material. The temperature was 13° C.

The results of these measurements are shown graphically in Fig. 1. It may be seen that the adiabatic curve corresponding to the highest rate of elongation has the least steep ascent, *i.e.*, at the highest rate of elongation the stress is greatest at a given elongation. With increase in the time of stretching, the curves approach nearer and nearer to the isothermal stress-strain curve. This would seem to prove that the rate of elongation plays an important part, wholly independent of any thermodynamic effects. Perhaps during rapid stretching there is actual rupture of chains which are still coiled and which mutually obstruct the smooth course of the stress-strain curve. It can also be seen from the position of the curves that the decisive effect shown by the time factor is of the order of seconds, since the difference between the curves corresponding to 0.68 and 2.5 seconds is very small, whereas the difference between the curves corresponding to 2.5 and 5.7 seconds appears to be considerable.

NOTE

The attention of the authors has been called by P. A. Thiessen to the fact that in a preliminary communication in 1935 (*Z. physik. Chem.* [B] **29**, 359(1935)) he and W. Wittstadt pointed out the importance of time effects in the arrangement of molecular chains after stretching, and further that the same subject was touched on by Wittstadt at a meeting of the chemistry teachers of Northwest Germany in 1938 (see *Z. angew. Chem.* **51**, 178(1938)).

Although certain principles common to the time effect described by Thiessen and Wittstadt have been assumed in the present work, the effect described appears

* Translated for Rubber Chemistry and Technology from Naturwissenschaften, Vol. 26, No. 21-22, pages 365-366, May 27, 1938; No. 28, page 461, July 15, 1938.

under quite different conditions. Since the title of the present communication might give rise to misunderstandings, we suggest another title for this new paper, namely, "The Influence of the Rate of Stretching on the Stress-Strain Curves when Stretching is Rapid."

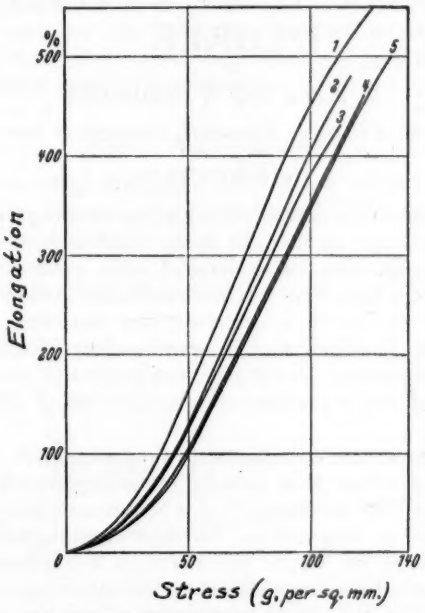

FIG. 1.—Stress-strain curves for different rates of elongation.

Curve 1. Isotherm.
Curve 2. 9.1 seconds' duration.
Curve 3. 5.7 seconds' duration.
Curve 4. 2.5 seconds' duration.
Curve 5. 0.68 seconds' duration.

THE DEPENDENCE OF THE STRESS ON THE TEMPERATURE OF RUBBER ELONGATED TO A CONSTANT DEGREE *

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INTRODUCTION

It is a recognized fact that rubber differs in its elastic properties from nearly all other elastic substances in that its elastic coefficient increases with rise in temperature, whereas the converse is true of other substances. This property of rubber has led to the idea that thermodynamically rubber may be compared with a gas, and that the elasticity of rubber is a statistical effect analogous to the elasticity of gases. This view was first expressed by Wöhlisch[1] and by Meyer and Ferri[2] and at the present time it has been fairly well established by a large number of theoretical and experimental investigations of Meyer, Ferri, Mark, Kuhn and others[3].

One of the most important conclusions to be drawn from these views is that the stress in elongated rubber must increase in direct proportion to the temperature, in the same way that the pressure of a gas maintained at constant volume increases with increase in temperature. An experimental proof of this necessary conclusion was furnished by Meyer and Ferri[2] in a fundamental investigation. In the experiments of these investigators, stress-strain curves of rubber were obtained by means of a Polanyi dynamometer at various temperatures; from these curves the changes in stress as a function of temperature at various definite elongations could be derived. In this way it was proved that the stress in a vulcanizate with a high sulfur content increased linearly with increase in temperature, and consequently that the relation: $\delta = aT + b$, expressed very closely the stress as a function of temperature. This simple proportionality between stress and temperature did not hold true of a vulcanizate with a low sulfur content, and the stress-temperature curve followed an irregular course, with evidence of retardation phenomena. Meyer and Ferri compared the behavior of weakly vulcanized rubber with the behavior of a true gas and the behavior of thoroughly vulcanized rubber with that of an ideal gas. In view of the fact that after weakly vulcanized rubber has reached a certain elongation it crystallizes very readily, and additional stresses are set up as a result of this crystallization, it is easy to explain the irregular course of the stress-temperature curve merely on the basis that the beginning of crystallization is influenced to a great extent by the temperature. It was on this same basis that Ornstein, Eymers and Wouda[4] found that in the case of raw rubber the stress decreased with increase in temperature, and further that Hauk and Neumann[5] found, in the case of weakly vulcanized rubber stretched only to low degrees of elongation, that there was no significant relation between stress and temperature, whereas at higher degrees of elongation this relation was strongly negative.

* Translated from the Zeitschrift für Physikalische Chemie, Abteilung A, Vol. 182, No. 4, pages 285-294, August 1938.

In all the investigations to which reference has been made, the stress-temperature curves were obtained from data on isothermal elongation at various temperatures. In view of this, it also seemed of interest to measure directly stresses at constant elongation as a function of temperature and at the same time, in the case of weakly vulcanized rubber, to eliminate to the greatest possible degree the phenomena of crystallization. This was the chief aim of the investigation to be described. In this work it seemed advisable to use samples the compositions of which were known as precisely as possible, and to include in the investigation various types of vulcanizates.

EXPERIMENTAL DATA

As a means of measuring stress as a function of temperature, the apparatus shown schematically in Figure 1 was constructed. This apparatus was operated in the manner described below.

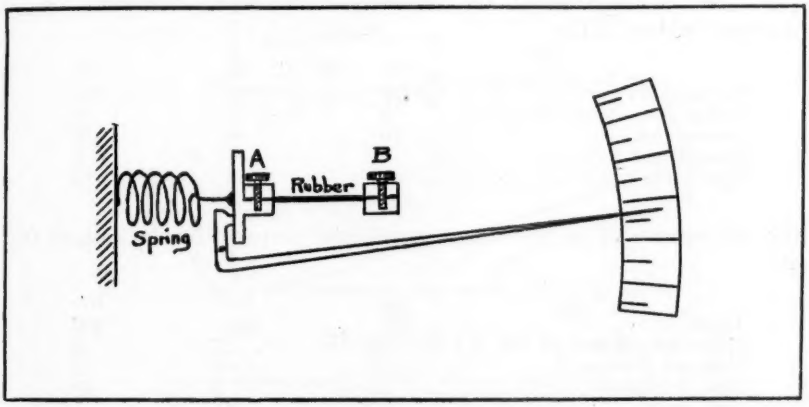

FIG. 1.—Instrument for measuring stress.

The sample strip of rubber, stretched between clamps A and B, adjustable to any degree of elongation by movement of clamp B, acted on a spring of such dimensions that its modulus of elasticity exceeded several fold that of the rubber sample. Under these conditions, changes in stress in the rubber sample did not either expend or contract the spring to any significant extent, so that the degree of elongation remained practically unchanged. However, these quite inappreciable movements of the spring were transmitted by means of a needle pointer so that they could be easily read on a scale.

The apparatus was calibrated by loading the spring with different weights, so that changes in stress of the sample of rubber elongated in the clamps could be read directly. As a means of studying the effect of temperature, the whole apparatus was placed in an air thermostat provided with a glass window so that the movement of the pointer could be observed from without. Measurements were carried out within the temperature range of 20° to 70° C. The temperature was raised each time about 10° C. and was maintained constant for 5 minutes to give the rubber an opportunity to come to temperature equilibrium. With a view to suppressing to the greatest possible extent all complicating phenomena of crystallization, the measurements were made only after the elongated rubber

samples had first of all been heated to 70° C. and then cooled before testing. Under these conditions the crystals which were formed during stretching melted, and consequently at 70° C. the stresses in the rubber were not modified by crystallization phenomena. Even if part of the rubber gradually crystallized again on cooling, this did not have a disturbing influence on the results, since no additional stresses were set up under these conditions. The true relation between stress and temperature was not determined until after warming and then cooling, and it was proved that under these conditions the stress-temperature relation was identical in both directions.

Three types of vulcanizates were investigated:

(1) Two vulcanizates, furnished for the purpose by the Semperit A.-G., which were prepared from crepe and 8 per cent of sulfur (with no other ingredients) and were vulcanized for two different lengths of time (60 and 90 minutes, respectively), *i.e.*, so that one vulcanizate (Ia) contained 2% combined sulfur, and the other vulcanizate (Ib) contained 6% combined sulfur.

(2) Three vulcanizates, of the following compositions, furnished by the Hungarian Rubber Works:

	IIa	IIb	IIc
Crepe	100	100	100
Sulfur	2	5	8
Accelerator	10	10	10
Stearic acid	1	1	1
Zinc oxide	5	5	5

(3) Vulcanizates of the following compositions, prepared by the authors from latex:

	IIIa	IIIb	IIIc
Latex	200	200	200
Colloidal sulfur	0.9	2.7	6
Vulkazit P extra N	0.3	0.9	2
10% Vulkamol	2.5	7.5	10
Zinc oxide	0.25	0.75	1.6

These latex mixtures were stirred, poured onto horizontal glass plates, allowed to dry, and the resulting films vulcanized for 30 minutes in hot air at 110° C.

EXPERIMENTAL RESULTS

Vulcanizates of Group I

Figure 2 shows the relation between stress and temperature in the case of vulcanizates of group I when stretched to various degrees, and determined by the apparatus described above. It is evident at once that the relation is a linear one, both for the weakly and strongly vulcanized samples.

To determine the stress-temperature coefficient and to prove conclusively that it was constant, the slope of the stress-temperature line, $d\delta/dT$, was plotted against the initial stress. Since $\frac{1}{\delta_0} \cdot \frac{d\delta}{dt} = \alpha$, the slope of the line thus obtained represented the stress-temperature coefficient, and the fact that a straight line was obtained is in itself proof of the constancy of this coefficient.

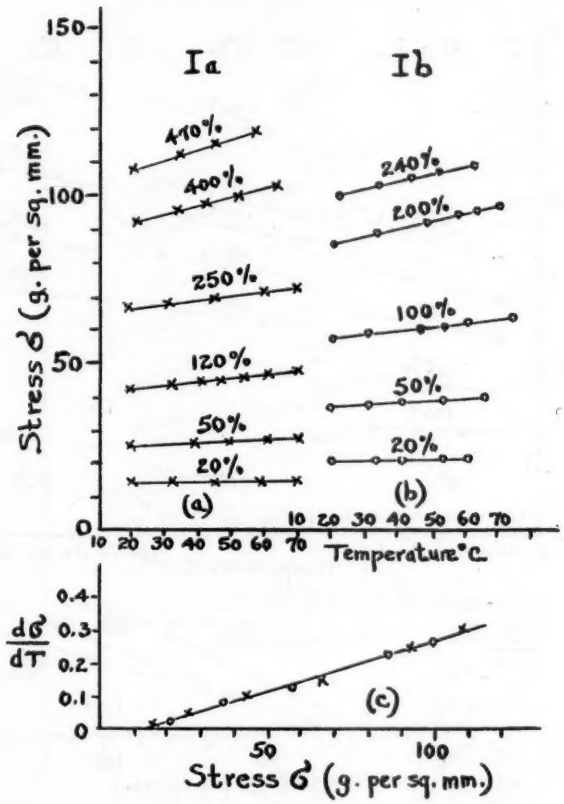

FIG. 2.—Vulcanizates Ia and Ib. Stress at constant elongation as a function of temperature.

Figure 2c gives the results for the two vulcanizates of Group I. It is evident that both vulcanizates had the same stress-temperature coefficient, the points representing the strongly and weakly vulcanized rubber samples falling on the same straight line.

VULCANIZATES OF GROUP II

Figures 3a, 3b and 3c show the relations between stress and temperature for the vulcanizates containing 2, 5 and 8 per cent, respectively, of sulfur, and Figure 3d shows $d\delta/dT$ as a function of δ_0 for these same three vulcanizates.

It is evident that in this case the stress-temperature coefficient was not independent of the degree of vulcanization, but that the vulcanizate of the lowest degree of vulcanization had the largest stress-temperature coefficient.

VULCANIZATES OF GROUP III

Figures 4a, 4b, and 4c show the relations between stress and temperature for the latex vulcanizates, and Figure 4d shows $d\delta/dT$ as a function of δ_0 for these

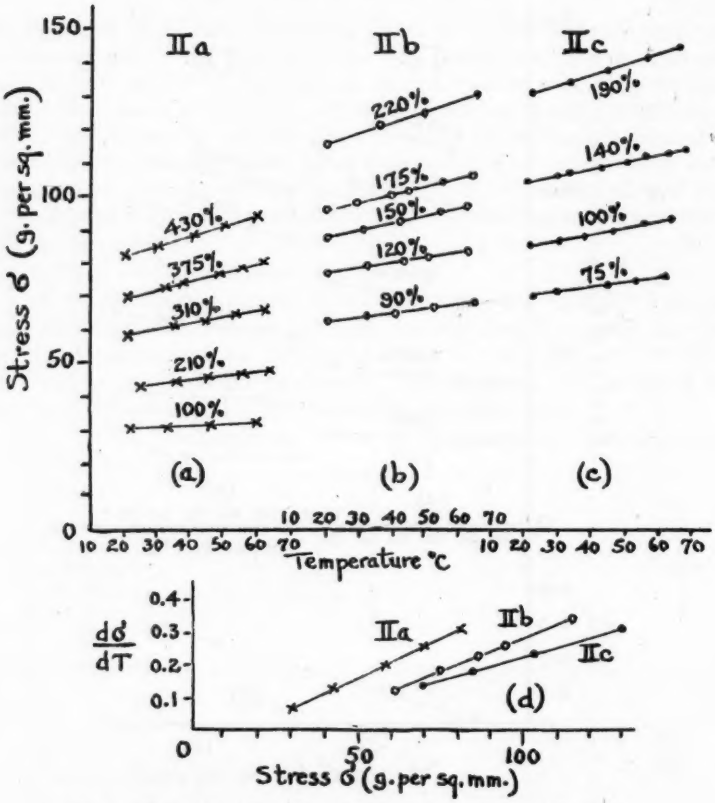

FIG. 3.—Vulcanizates IIa, IIb and IIc. Stress at constant elongation as a function of temperature.

same vulcanizates. Here the most noteworthy result was that the change in stress with change in temperature was especially great for low states of vulcanization and at high elongations. Also the changes in the stress-temperature coefficients were peculiar, for at low elongations the coefficients of all three vulcanizates were the same, whereas at higher elongations the coefficients of the different vulcanizates followed different trends; the coefficient of the most weakly vulcanized sample changed to the greatest extent and its ultimate value was the greatest of all.

DISCUSSION OF THE RESULTS

The experimental results just described lead to two conclusions: (1) that in every case the stress increased in proportion to the increase in the absloute temperature, and (2) that at relatively high elongations the stress-temperature coefficient was a function of the state of vulcanization, *i.e.*, it decreased with increase in sulfur content.

In the formula: $\delta = at + b$, which represents stress as a function of temperature, the two constants a and b are of definite significance, in that $a = -(\partial S/\partial D)_T$ and $b = (\partial U/\partial D)_T$. where D is the percentage elongation, S is the entropy and U is

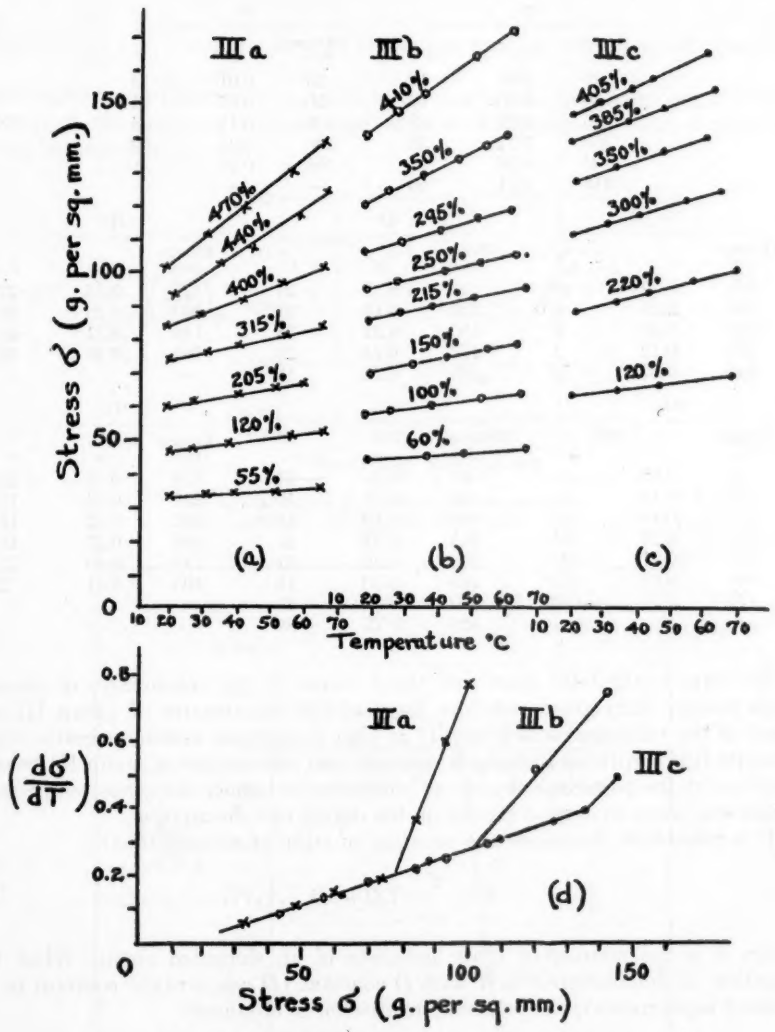

FIG. 4.—Vulcanizates IIIa, IIIb and IIIc. Stress at constant elongation as a function of temperature.

the internal energy. Therefore in the case of an ideal rubber analogous to an ideal gas, the relations: $(\delta U/\delta D)_T = b = 0$, would necessarily hold, since no change in internal energy would occur during stretching. The a values can be read directly from the stress-temperature curves, and the b values can be readily obtained by extrapolation.

The following table gives the a values and b values obtained in this way for the three groups of vulcanizates elongated to different degrees. In these tables the elongations are expressed in percentage, a expressed in grams per sq. mm. per degree and b in grams per sq. mm.

Ia			Ib		
Elongation	a	b	Elongation	a	b
20	0.01	+ 12	20	0.01	+ 4
50	0.05	10	50	0.07	21
120	0.09	16	100	0.13	38
250	0.12	33	200	0.23	69
400	0.26	17	240	0.24	71
470	0.31	16	—	—	—

IIa			IIb			IIc		
Elongation	a	b	Elongation	a	b	Elongation	a	b
100	0.32	+ 10	90	0.13	+ 24	75	0.14	+ 27
210	0.25	8	120	0.19	21	100	0.20	27
310	0.20	0	150	0.22	23	140	0.21	44
375	0.12	− 3	175	0.24	25	190	0.30	43
430	0.07	− 12	220	0.35	12	—	—	—

IIIa			IIIb			IIIc		
Elongation	a	b	Elongation	a	b	Elongation	a	b
55	0.05	+ 18	60	0.08	+ 21	120	0.14	+ 23
120	0.11	15	100	0.14	16	220	0.26	13
205	0.16	13	150	0.19	13	300	0.32	17
315	0.21	12	215	0.22	21	350	0.37	18
400	0.37	− 25	250	0.25	22	385	0.40	22
440	0.63	− 93	295	0.30	16	405	0.51	− 2
470	0.77	− 122	350	0.53	− 35	—	—	—
—	—	—	410	0.77	− 86	—	—	—

The data in the table show that the b values of the vulcanizates of group I were positive throughout, whereas those of the vulcanizates of group III and those of the vulcanizates of group II at high elongations became negative. Incidentally it is surprising that the b values of the vulcanizates of group III became negative at the particular degrees of elongation at which the stress-temperature coefficient began to depend greatly on the degree of vulcanization.

It is possible to formulate the equation of state of rubber[6] thus:

$$\delta = \frac{a'}{\sqrt{n}} TD + bD \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where n is the number of chain members of an elongated chain. When this equation is differentiated for T with D constant (D was actually constant in the present experiments), the following expression is obtained:

$$\frac{d\delta}{dT} = \frac{a'}{\sqrt{n}} D$$

Replacement in this equation of the value of D in equation (1), gives the equation:

$$\frac{d\delta}{dT} = \frac{a'}{\sqrt{n}} \cdot \frac{\delta}{\frac{a'}{\sqrt{n}} T + b}$$

or in transposed form:

$$\frac{d\delta}{dT} \cdot \frac{1}{\delta} = \frac{a'}{a'T + \sqrt{n} \cdot b}$$

However, $\frac{d\delta}{dT} \cdot \frac{1}{\delta}$ is nothing but the stress-temperature coefficient and therefore is obviously independent of n; n, which is the number of chain members, naturally depends on the degree of vulcanization, since with increase in sulfur content the chains become shorter.

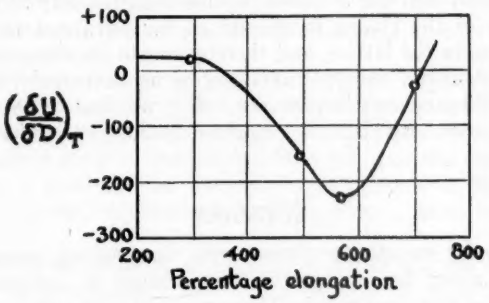

FIG. 5.—$(\delta U/\delta D)_T$ as a function of the elongation, according to Wiegand and Snyder.

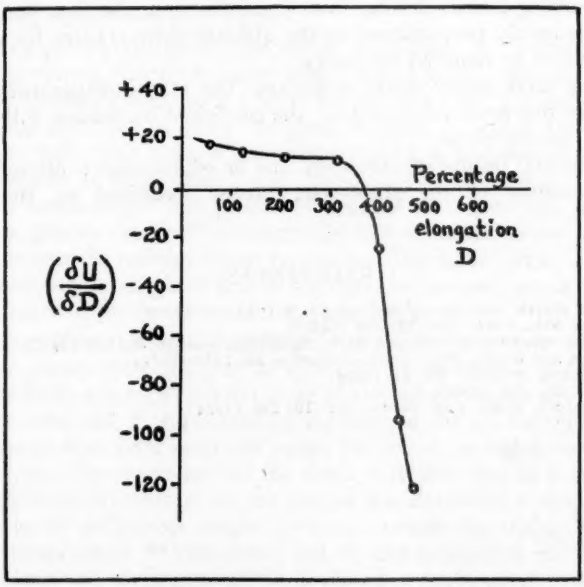

FIG. 6.—Vulcanizate IIIa (see Table III). $b = (\delta U/\delta D)_T$ as a function of the elongation.

As a result, the stress-temperature coefficient at relatively large values of n (low degrees of vulcanization) can increase only when the b values become negative. The table shows that the b values for the vulcanizates of Group III and for those of Group IIa at high degrees of elongation actually did become negative. The constant b represents, however, nothing else than $(\partial U/\partial D)_T$. Wiegand and Snyder[7] likewise derived a negative value for the function $(\partial U/\partial D)_T$ at relatively

high degrees of elongation, as may be seen in Figure 5. When the b values obtained in the present work are plotted against the elongation, they follow the same general course as do those of Wiegand and Snyder, as is evident by a comparison of Figures 5 and 6.

The change of the b values to negative indicates however that there is in rubber a force which tends to elongate the rubber. This is easily understood when it is considered that the b values become negative only at high elongations, when orientation of the chains is already so far advanced that they tend to arrange themselves in the lattice, and thereby create an elongating force. When crystallization is complete, the $(\partial U/\partial D)_T$ values again increase, as is evident also in the curve of Wiegand and Snyder (*loc. cit.*), whereas the values obtained in the present work naturally could not increase because all tendency to crystallize was eliminated.

SUMMARY

An instrument for measuring stresses was constructed, whereby changes in tension brought about by changes in temperature in rubber maintained at constant elongation were measured. These measurements were carried out with three types of vulcanizates.

After measures were taken in the case of weakly vulcanized samples to eliminate the disturbing factors arising from crystallization, the fact was established that stress is directly proportional to the absolute temperature for all types of vulcanized rubber, as required by theory.

It is shown that under some conditions the stress-temperature coefficient depends on the degree of vulcanization, the coefficient decreasing with increase in the degree of vulcanization.

The experimental results are discussed, and an explanation is offered to account for the dependence of the stress-temperature coefficient on the degree of vulcanization.

REFERENCES

[1] Wöhlisch, *Verh. physik. med. Ges. Würzburg* [N. F.], **51**, 53 (1936).
[2] Meyer and Ferri, *Helv. Chem. Acta* **18**, 570 (1935).
[3] See the literature references of Guth and Mark, *Naturwissenschaften* **25**, 353 (1937).
[4] Ornstein, Eymers and Wouda, *Proc. Acad. Amsterdam* **32**, 1235 (1929).
[5] Hauk and Neumann, *Monatsh.* **72**, 32 (1938).
[6] Pelzer, *Monatsh.* **71**, 444 (1938).
[7] Wiegand and Snyder, *Trans. Inst. Rubber Ind.* **10**, 284 (1934).

AN IMPROVED WIEGAND RUBBER PENDULUM *

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A heat engine with rubber as the working substance was invented some years ago by Wiegand[1] and called the rubber pendulum. By virtue of the Joule effect (the increase in tension of stretched rubber with increase of temperature) heat energy absorbed by a strip of rubber is converted into the mechanical energy necessary to keep a pendulum in motion. Improvements in the design of the pendulum and a detailed consideration of the theory have been given more recently[2].

In the course of construction of an apparatus of this sort for exhibition at the National Bureau of Standards it was found possible to make certain material simplifications and improvements, which may be of interest to those planning a demonstration or study of the rubber pendulum. The major features are (1) an improvement in mechanical stability, (2) a decrease in size and weight, and (3) considerable simplification of parts.

Fig. 1 shows a photograph of the new rubber pendulum. An ordinary laboratory stand, *A*, holds a ring-clamp, *B*, upon which are mounted two steel knife-edge bearings. The oscillating element is a brass rod about 0.8 cm. ($\frac{5}{16}$ in.) in diameter and 60 cm. long, threaded to carry two brass weights, *C*, which are displaceable along its upper half. The weights are cylinders with a diameter of about 5 cm. (2 in.) and lengths of 6 cm. and 3 cm., respectively. The use of two weights, rather than a single larger one, makes it possible to adjust the pendulum to operate over a greater range of tension in the rubber bands, as one or the other of the weights may be omitted when necessary. The knife edges, *D*, are made by filing a 3-mm. steel rod, which is then inserted and soldered into a hole running through the center of the brass rod and at right angles to it.

The restoring force for the pendulum is obtained from two rubber bands hooked over a 3-mm. steel rod passing through the lower end of the brass rod parallel to the knife edges. The lower ends of the rubber bands are hooked over another 3-mm. steel rod, *E*, supported by a clamp on the laboratory stand. This rod also carries an aluminum sheet, the upper portion, *F*, of which serves as shield for the heat rays. The lower end of the sheet is folded over so that the rod *E* passes through it at two points. In the fold of the aluminum a strip of metal is laid to serve as an adjustable weight to keep upright the triangular shield *F*. The shield extends about 20 cm. above rod *E*, and is about 5 cm. wide at the top. Close behind the aluminum shield is placed a single small radiant heater, consisting of a 550-watt electric heating element with reflector.

Compared with the previous design of the rubber pendulum, the present model has the shield inverted and the stretched rubber bands exert their restoring force as a downward, rather than as an upward, pull on the moving element. Because of this change the rubber bands no longer tend to lift the knife edges out of their supports, and there is no necessity for weights at the lower end of the brass rod. Furthermore, since one rubber band is placed in front of the brass

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rod and one behind it, their pulls are symmetrical, so that equal loads are supported by the two knife-edges.

Rubber bands of several different types have proved satisfactory. Those most commonly used are No. 11 pure-gum bands about 8 cm. in circumference. With these bands, operation is possible at elongations of less than 90 per cent, although higher elongations give better performance. Under the conditions of Wiegand's experiments he found operation impossible below a critical elongation slightly less than 300 per cent.

FIG. 1.—Improved Wiegand rubber pendulum.

In order to set the pendulum in operation, the lower rod, *E*, is set to give the bands the desired elongation, usually three hundred or four hundred per cent. The brass weights are so placed that the pendulum is slightly top-heavy, so that it will come to rest on one side or the other and not in the center. Centering of the swing of the pendulum in order to obtain equal amplitudes on each side of the center is brought about by slight displacements of rod *E* in a horizontal plane. The aluminum shield is brought to the center of the arc of the pendulum, if necessary, by a shift of the metal weight in the fold of the aluminum. Finally the heater is placed behind the shield.

If the adjustments have been properly made, oscillations of the pendulum should begin. The heat absorbed by the bands raises their temperature, and an

increase in tension of the bands ensues. This brings the pendulum nearer the center of its stroke, and brings the bands into the shadow of the aluminum screen. Here the temperature falls and the tension decreases. When the kinetic energy of the moving mass becomes sufficient to carry the pendulum past the center, the bands emerge from the shadow of the screen on the opposite side, and the whole process is repeated. The period of the pendulum may be varied by a displacement of the weights, by a change in the size of the shield, or by a change in the elongation of the rubber bands. By any of these methods the change in temperature of the bands may be made very rapidly, and a complete cycle of heating twice and cooling twice may require as little as four or five seconds.

After a short period of operation a readjustment of the brass weights may be required, but after that no further attention is usually demanded. A pair of rubber bands often survives several weeks of operation, eight hours each day.

It has also been found possible, as Wiegand discovered, to operate with the pendulum bottom-heavy, by lowering the weights so that in the absence of the heater the pendulum would come to rest in the center of its swing in a vertical position, rather than in a position inclined to the vertical. In this case, of course, it is necessary to start the oscillations by hand.

REFERENCES

[1] Wiegand, *Trans. Inst. Rubber Ind.* **1**, 141 (1925).
[2] Wiegand and Snyder, *Trans. Inst. Rubber Ind.* **10**, 234 (1936); Rubber Chem. Tech. **8**, 151 (1935).

NOTE ON THE THEORY OF WATER ABSORPTION BY RUBBER *

H. A. DAYNES

There is still a need for a quantitative theory of the form of curves describing the changes of water content of rubber with time of exposure to various conditions of ambient humidity. Although considerable progress has been made in recent years, both in our understanding of the factors which determine such curves and in the use of empirical relations, there is still no fundamental solution which will enable reliable predictions to be made either for practical purposes or for verification of theories of the mechanism of absorption.

It has been shown that, although this problem has much in common with that of the conduction of heat in solids, the chief obstacle to the application of the latter theory is the great deviation from linearity in the relation between humidity and the concentration of water in rubber which is in equilibrium with that humidity. It was also realized that it could not be assumed that the diffusion constant was independent of concentration (Daynes, *Trans. Faraday Soc.*, **33**, 531 (1937)).

Blake and Morss (*Proc. Rubber Technology Conference*, London, **1938**, 868), making use of this analogy between diffusion and heat conductivity, applied the well known differential equation:

$$\frac{\partial u}{\partial T} = \frac{1}{a^2}\left(\frac{\partial^2 u}{\partial l^2}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

to the case of water diffusion, taking u to be the concentration of water and a^2 the ratio of the specific solubility to the diffusion constant. They proposed to take account of both the variable factors mentioned in the preceding paragraph by expressing a as an experimentally determined function of vapour pressure.

The equation quoted is, however, derived by differentiation from Fick's Law on the assumption that both the diffusion constant and the specific solubility are constant, so that it is inadmissable merely to introduce these as variables in the derived equation.

The effect of a variable diffusion constant corresponds to that of a variable conductivity in the heat conduction case, and is considered in various textbooks (*e.g., Carslaw's Mathematical Theory of the Conduction of Heat in Solids*). The heat conduction case in which both conductivity and specific heat are variable has been considered by Peek (*Physical Review*, **35**, 554 (1930)), who clearly pointed out the conditions of applicability of his equation to the case of diffusion.

For the particular case of water diffusion in rubber it has been shown (Daynes, *loc. cit.*) that, according to the osmotic theory, this form of equation holds only if the independent variable u represents the relative vapor pressure (not the concentration), the diffusion constant being independent of humidity.

Awbery (*Proc. Phys. Soc.*, **48**, 118 (1936)) has dealt with the analogous case of temperature variation in a material of which the thermal properties vary with temperature. The only case for which he obtains an exact solution is that in which the conductivity and the specific heat vary linearly with temperature and in

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 14, No. 3, pages 191-193, October 1938.

constant ratio. A more general solution was obtained by an approximation method, assuming that the variations of thermal properties were small. Unfortunately, neither of these conditions applies even approximately to the diffusion of moisture into rubber, but some use may be made of Awbery's method of treatment.

Consider a unidimensional case of diffusion parallel to the axis of x.

Let Q = rate of diffusion of water across unit area at x, at time t,
h = relative humidity at x,
D_h = diffusion "constant" at a humidity h,
S_h = "specific solubility" at a humidity h, *i.e.* the rate of change of concentration with humidity.

Then, if Fick's Law holds in the form:

$$Q = -D_h \frac{\partial h}{\partial x},$$

it can be shown that:

$$S_h \frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(D_h \frac{\partial h}{\partial x}\right) = D_h \frac{\partial^2 h}{\partial x^2} + \frac{\partial D_h}{\partial h}\left(\frac{\partial h}{\partial x}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots (2)$$

This is equivalent to Peek's Equation (3) and, if D_h is constant, reduces to the simpler case previously considered (Daynes, *loc. cit.*).

Following the method of Awbery, substitute a function y for $\frac{x}{(2t)^{\frac{1}{2}}}$ and so transform the partial differential Equation (2) into an ordinary differential equation, h becoming a function of a single variable. This transformation leads to:

$$S_h y \frac{dh}{dy} + D_h \frac{d^2 h}{dy^2} + \frac{dD_h}{dh}\left(\frac{dh}{dy}\right)^2 = 0 \quad \ldots\ldots\ldots\ldots\ldots (3)$$

S_h varies over a very wide range (of the order of 200 to 1) with h (Lowry and Kohman, *J. Phys. Chem.*, **31**, 23 (1927)). Evidence as to the variation of diffusion constant with h has been given by Taylor, Herrmann and Kemp (*Ind. Eng. Chem.*, **28**, 1255 (1936)), who found that the rate of diffusion through a thin sheet was proportional to the difference of humidity up to about 75 per cent. relative humidity. The ratio then increased by an amount which rose to about 15 per cent. at 100 per cent. humidity. The value of their diffusion constant is not the exact equivalent of D_h, as it is an effective mean over the whole range of humidity between the two sides of the sheet. The variation in D_h is therefore somewhat greater than is indicated by their curve, but the correction for this difference cannot be calculated from their data. For example, in their Table I, the value for their "diffusion constant" for a range 23.6 to 17.8 mm. mercury is higher than that for a range 23.6 to 0 mm. mercury, as would be expected. Taylor, Herrmann and Kemp in the same paper recorded an experiment to determine the actual distribution of moisture through a laminated sheet during equilibrium conditions of diffusion, and showed that the distribution agreed with that calculated on the assumption of a uniform pressure gradient through the sheet. If there had been serious variation of D_h this agreement would not have been obtained, because under equilibrium conditions the pressure gradient would be inversely proportional to the diffusion constant at all points.

If the variation in D_h is neglected, Equation (3) reduces to:

$$S_h y \frac{dh}{dy} + D \frac{d^2h}{dy^2} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

In the absence of even an approximate solution of Equation (4) it seems premature to introduce the complication of the variability of D_h. With a solution of (4) it should be possible to take into account the variation of D_h by approximation methods.

Incidentally, it may be pointed out that Equations (3) and (4) are consistent with the rule that the times required to reach similar stages of saturation in sheets of different thicknesses are proportional to the square of the thickness.

SOME PRACTICAL ASPECTS OF THE THEORY OF DIFFUSION OF WATER THROUGH RUBBER *

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PRACTICAL FIELD OF INTEREST OF THE SUBJECT

The rate of passage of moisture through rubber and the amount absorbed by it are of practical importance in the production and applications of the material, as illustrated by the following examples:

(1) In the preparation of raw rubber, the rate of drying is one of the important factors in production cost.

(2) In electrical signalling cables, the demand for low dielectric constant and power factor, which are adversely affected by absorbed moisture, is becoming more severe with the increase in audio and carrier frequency transmission. The rapid increase in the last few years in the use of Paragutta, which contains deproteinized rubber, in place of gutta-percha in submarine cables is evidence of the value of the purification of rubber for such purposes[1].

(3) The absorption of water by the rubber insulation of lighting and power cables has led to serious trouble under certain conditions which arise in modern buildings.

(4) The power factor of ebonite to be used at radio-frequencies is very sensitive to slight traces of moisture.

(5) The rapid removal of water is important in most processes for the production of articles directly from rubber latex.

(6) The swelling and loss of mechanical strength due to absorbed water are objectionable, for example, in many mechanical goods, steam packings and hot-water bottles.

(7) The diffusion of moisture through thin films has received attention recently in connection with packaging materials and other thin films[2].

TIME RELATIONS IN ABSORPTION AND DIFFUSION

At one time interest in the subject was confined largely to the amount of moisture absorbed under equilibrium conditions, *i.e.*, when the rubber is saturated; but these conditions seldom arise except with very thin films. More recently attention has been given to time relations before the establishment of equilibrium or to the gradient of moisture concentration within the rubber while diffusion is proceeding. The problem occurs in various forms according to the application in question.

(1) *Initial rate of absorption.*—The measurement of the amount of water absorbed during a comparatively short immersion is frequently used as a test of rubbers for service under wet conditions. It is important to consider to what extent such short period tests can represent relative merits after long immersion.

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(2) *Absorption and desorption during longer exposures.*—The intermediate period between the initial stage, in which absorption is proportional to the surface exposed, and the final equilibrium stage, when absorption is proportional to the volume, is one in which the form of time-absorption curve depends on the shape and size of specimen, and the mathematical treatment of the problem is difficult in the case of all but the simplest shapes. Nevertheless, this intermediate phase in both absorption and desorption is of great practical importance, as may be seen from the following examples:

(*a*) In the drying of rubber the processes should be stopped when the water content has been reduced to a certain limit. Complete drying would be unnecessary and therefore wasteful, since water would be regained to some extent on exposure to the atmosphere.

(*b*) In the storage of unvulcanized mixed stocks, the regain of moisture after milling should be limited if porosity during certain vulcanization processes is to be avoided.

(*c*) In open-steam vulcanization there are chemical changes of technical importance in the non-hydrocarbon components of the rubber, which may be attributed to reactions with steam which has diffused into the rubber.

(*d*) In testing the rate of water absorption by rubber, it is often difficult to obtain sufficient accuracy without carrying the absorption beyond the initial "surface" phase, in which case the interpretation of the results is difficult.

(3) *Exposure to periodic changes of humidity.* When rubber is exposed to an atmosphere of fluctuating humidity, the extent to which the inside portions are affected depends on their depth below the surface and on the frequency of the fluctuations. Such cases occur, for example, with insulating materials in the tropics, where there is a heavy condensation at times, or in industrial installations where intermittent exposure to steam or hot water may occur.

(4) *Distribution of moisture through the rubber.*—In any experimental investigation of diffusion of water in rubber it is usually the total absorption or the rate of permeation which is measured. In order to interpret the results completely, it is necessary to be able to calculate the concentration at each part of the rubber as a function of time, unless equilibrium is reached.

There are also various practical cases in which the distribution of moisture is of more importance than the average concentration. Cases dealing with the drying of rubber and the use of insulating materials will be discussed in detail in the last section of this paper.

BASIS OF MATHEMATICAL THEORY OF DIFFUSION

The solution of such problems as are exemplified above requires the establishment of a differential equation of diffusion within the rubber, and several workers have naturally made use of the analogy with other diffusion processes. On the basis of published evidence that Fick's law is applicable, the rate of diffusion being proportional to the gradient of vapor pressure, the equation adopted has been[3]:

$$\frac{\partial c}{\partial t} = K \frac{\partial^2 c}{\partial x^2} \qquad \text{.....(1)}$$

where c is the concentration of moisture at time t and at a point defined by x. On this assumption it has been predicted that the time required for a sheet of rubber to reach a given degree of saturation is proportional to the square of its thickness, and there is experimental verification of this prediction[3].

It has been shown by the author, however, that this equation (1) is not correct, and gives misleading conclusions in other respects[4]. The reader is

referred to the original paper for the full evidence and argument but, briefly, the error arises from the fact that Henry's law does not apply here as it does in other diffusion cases, the concentration of water not being even approximately proportional to vapor pressure (Fig. 1). The differential equation has to be modified to:

$$\frac{\partial h}{\partial t} \cdot \frac{\partial c}{\partial h} = D^1 \frac{\partial^2 h}{\partial x^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where h is the relative humidity in equilibrium with the rubber containing water at a concentration c. Thus $\frac{\partial c}{\partial h}$ is the slope of the water concentration/relative humidity curve, and its value may vary over a range of the order of 200 to 1, particularly at the higher humidities.

If the simpler equation (1) had been correct, it would have been possible to make use of the highly developed theory of conduction of heat, which conforms

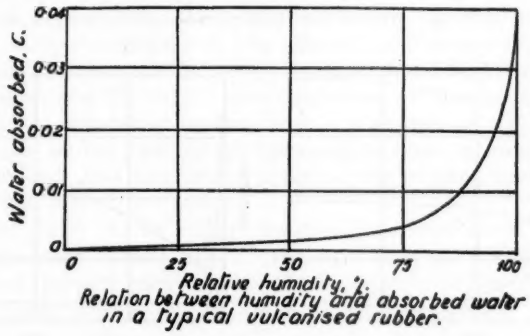


FIG. 1.

to a similar differential equation. The case according to Equation (2) would be analogous to the conduction of heat in a material of which the specific heat varied greatly over the upper part of the temperature range.

ABSORPTION AND DESORPTION CURVES ACCORDING TO THE NEW THEORY

The contrast between absorption and desorption curves according to Equations (1) and (2) is illustrated by Figures 2 and 3.

In Figure 2, A and B represent gaseous absorption according to Equation (1) by a sheet exposed to partial gas pressures of 1 and 0.5 atmosphere, respectively, and C is the desorption curve from a sheet saturated at 1 atmosphere and then exposed to a vacuum. It is seen that A is similar to B except that the ordinates are everywhere doubled, the time constants of the curves being the same, and C is the inverse of A.

In Figure 3, A and B represent water absorption according to Equation (2) by a sheet in atmospheres of 100% and 50% relative humidity, respectively, and C is the drying curve of a sheet initially saturated at 100% relative humidity. It is seen that the heights of the asymptotes of A and B are in a ratio much greater than 2 to 1, the curves are different in shape, and their time constants are different. The drying curve is of a different shape from the wetting curve and equilibrium is approached more quickly.

The conclusions from Equation (2) may be summarized thus:

(1) The thickness-square law of time to reach a certain degree of saturation holds just as for Equation (1).

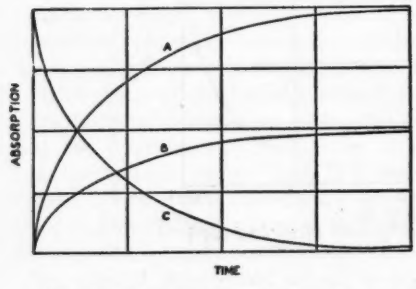
(2) The higher the vapor pressure to which the rubber is exposed and the greater the hygroscopicity of the rubber, the longer is the time to reach equilibrium.

(3) At high humidities the absorption graph is sharply curved at first, and there is a very prolonged approach to saturation.

(4) On the other hand, the drying curve is almost straight at first and abruptly curved to a fairly sharp end-point, which is reached in a time much shorter than that required for saturation.

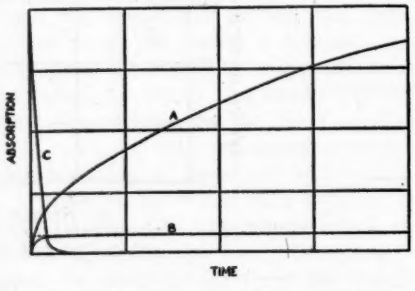
(5) The narrower the limits of humidity between which the changes take place, the more nearly do the absorption and desorption curves conform to Equation (1), since $\frac{\partial c}{\partial h}$ is more nearly constant.

(6) The time scale of absorption and desorption curves is determined also by the diffusion constant within the rubber (D^1 of Equation 2).



Gas absorption according to Equation (1).

FIG. 2.



Water absorption according to Equation (2).

FIG. 3.

SOME CONSEQUENCES OF PRACTICAL IMPORTANCE

It is impossible to indicate all the practical significance of this theory of diffusion, but it is proposed to discuss briefly three important aspects, namely: (1) the testing of rubber for water absorption; (2) the drying of raw rubber, and (3) changes in performance of electrical insulators during absorption.

(1) (*a*) The measurement of absorption at equilibrium on immersion in water has always been one of some difficulty. Very thin sheets are often difficult or impossible to prepare so as to be comparable in properties with a thicker sample of nominally the same rubber. Moreover, tests may be required on existing samples of unknown composition. With thick samples, the attainment of equilibrium is very slow, difficult to judge, and easily masked by the effects of oxidation. Consequently there have been attempts to estimate the ultimate absorption by tests in which samples of standard dimensions are immersed for a fixed time insufficient for saturation, *e.g.*, a day or two, and the amounts absorbed used as an indication of the relative merits of the samples.

The theory indicates that even if two rubbers have the same equilibrium absorption, the rates at which they take up water are affected by two other independent factors, the diffusion constant and the shape of the vapor pres-

sure/absorption curve. While these factors vary from one rubber to another and there is no complete mathematical solution of Equation (2) to guide us, it is not possible to regard these short period tests as other than empirical ones, applying only to rubber in service in pre-equilibrium conditions and of the shape and size actually tested. It is not suggested that such tests are of no value as comparative tests, but predictions based on them must be treated only as probabilities based on wide experience of such tests. The same remarks apply to such statements as that the form of the absorption curve is of the parabolic or the exponential type. The former is true up to half-saturation and the latter after half-saturation in gas diffusion according to Equation (1), but not necessarily when Equation (2) applies.

It has been shown that the time to reach half-saturation generally increases with the hygroscopicity of the rubber, *i.e.*, the half-saturation period increases with the height of the asymptote to the absorption curve[4]. There is, therefore, a tendency for short period tests to show less differences between rubbers than saturation tests.

It is known that there are appreciable differences in the diffusion constant of air in various rubbers according to the amount and nature of compounding ingredients used[5]. In the case of freshly coagulated rubber, it has been suggested by Stevens[6] and de Vries[7] that differences in rate of drying are determined largely by changes in permeability or structure of the coagulum. In the analogous case of the swelling of vulcanized rubber by organic liquids it has been pointed out[8] that the time constant of the swelling curve varies considerably from one rubber to another.

So far as the shape of the vapor pressure/absorption curve is concerned, the author's experience is that this shape varies very much from one rubber to another. Two rubbers may absorb equal amounts at, say, 75% relative humidity, and differ considerably at 100%; even crossing-over of the curves may occur.

(*b*) The fact that drying takes place much more quickly than saturating may be used to simplify testing technique. Rubbers may be stored in water for a long time in absence of oxygen and then weighed before and after drying instead of, as usual, before and after saturating. This method has some advantages: (1) the difference in weight is not subject to correction for water-soluble components extracted from the rubber; (2) the shorter interval between weighings reduces the risk of errors due to oxidation, and (3) the sharper approach to constant weight on drying is a practical convenience.

(*c*) In absorption tests the results are affected to an uncertain extent by the initial content of moisture in the sample, unless it is previously dried, and it is sometimes assumed that the time required for drying is comparable with that required for saturation. It has been shown that the time required is very much shorter.

(*d*) In investigating rubbers for service in aqueous solutions, such as sea water, or in atmospheres of less than 100% relative humidity, it is inadvisable to test in pure water. Apart from the fact that the results of water immersion tests may be misleading owing to the difference in vapor pressure from service conditions, the use of a solution of lower vapor pressure greatly reduces the period of the test and reduces the risk of errors due to oxidation.

(2) The drying of raw rubber is in many ways more complicated than that of vulcanized rubber; the structure of the fresh coagulum is probably different from that of dried rubber and changes with water content during the drying process; the starting point is not a condition of solution equilibrium

with the washing water, the initial water content being determined largely by the mechanical conditions of rolling, and chemical changes are continuously taking place in the non-rubber components. Attention has already been drawn by various writers to the influence of temperature, thickness of the sheet and possible changes in diffusion constant on the rate of drying[9], but little, if any, notice has been taken of the influence of the shape of the vapor pressure/absorption curve. The theory indicates that the best shape of curve for drying is one in which the water absorption falls away as steeply as possible when vapor pressure is reduced from 100% relative humidity, and this condition would probably be advantageous also in the finished rubber. The shape of the curve depends on the water absorption properties of the serum components, which can be altered by chemical treatment or bacteriological action, and it is suggested that past observations and plans for future research on drying should be re-examined from this standpoint.

(3) Even small traces of absorbed moisture have a marked effect on the electrical properties of insulating materials. According to the type of service, the absorption of water may lead to physical or electrical breakdown or to such deterioration in performance that the insulator is no longer serviceable.[10] As moisture penetrates inwards from the surface the various electrical properties progressively deteriorate, but the rate at which the performance is affected depends on which property is chiefly concerned, because these are affected differently by a given change in the distribution of moisture.

For example, in the case of a rubber-insulated cable the dielectric breakdown strength of the outer moist layer is reduced, but this is in the weakest part of the radial field so that little effect is expected for some time, except so far as the change in dielectric constant in the outer layer causes a readjustment of potential gradients through the rubber, and so applies greater stress in the central part of the field. We should expect that the effective power factor and dielectric constant would be affected appreciably in a short time, but that the insulation resistance change would be long delayed because the low resistance outer layers would be in series with the high resistance inner portion which remains dry for a long time.

On the other hand, in the case of two terminals set in the surface of an ebonite insulator, we should expect surface breakdown properties and insulation resistance between the terminals to be quickly affected, because the low resistance leakage path would now be in parallel with the dry inner portions of the insulator.

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REFERENCES

[1] *Siemens Mag.*, (Eng. Suppl.), Jan. and July (1936); Rosen and Crutch, *ibid.* Jan. (1938); Rosen and Smith, *ibid.* (1938).
[2] Taylor, Herrmann and Kemp, *Ind. Eng. Chem.* **28**, 1255 (1936).
[3] Andrews and Johnston, *J. Am. Chem. Soc.* **46**, 640 (1924); van Harpen, *Kautschuk* **7**, 108 (1931); Piddlesden, *J. Rubber Res. Inst. Malaya* **7**, 117 (1937).
[4] Daynes, *Trans. Faraday Soc.* **33**, 531 (1937).
[5] Morris, *Ind. Eng. Chem.* **23**, 837 (1931).
[6] *Rubber Age* (London) **7**, 502 (1926-27).
[7] *Arch. Rubbercultuur* **7**, 119 (1923).
[8] Scott, *Trans. Inst. Rubber Ind.* **5**, 95 (1929).
[9] van Harpen, *Kautschuk* **7**, 108 (1931); Piddlesden, *J. Rubber Res. Inst. Malaya* **7**, 117 (1937).

VULCANIZATION OF OXIDIZED RUBBERS *

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London

DESCRIPTION

A study of the vulcanization of oxidized rubber (Rubbone) brings out several interesting facts which may throw light on the vulcanization process generally. A description of the effect of vulcanization as applied to the oxidized products is necessary before proceeding to a discussion of the implications involved.

The catalytic oxidation of rubber, using cobalt linoleate as catalyst, has been described[1]. The three products separated by solvent action are not necessarily simple in character, but there is evidence that two of them at least, Rubbone A and B, are substantially homogeneous. The third, Rubbone C, has not been studied so completely.

They represent approximately atomic additions of oxygen to four isoprene units, two isoprene units and one isoprene unit, respectively. If vulcanization consists merely in adding sulfur to double bonds it would be anticipated that a reduction in the amount of combined sulfur would take place, consistent with the reduction of double bonds by oxygen, more or less in proportion to the oxygen added. Compare Spence and Scott[2], who determined the amount of bromine required to saturate the residual bonds of a soft vulcanized rubber. They found the relationship: $2Br_2=S_2$. This has proved to be the case with Rubbones A and B, but not with Rubbone C. The combined sulfur found in the product from this latter is nearly the same as in Rubbone B, and deoxygenation is suspected, since sulfur dioxide has been detected in the vulcanization reaction. In all cases full physical effects were obtained before the combination of sulfur had attained a maximum, and in the case of Rubbone C even before combination had begun. These effects, which may be described as vulcanization effects, differ from those obtained with rubber in so far that whereas stout gels are produced in the earlier stages and hard, brittle, slightly thermoplastic solids resembling hard rubber in the later stages, elastic highly distensible materials are not produced.

There is a possibility that unchanged Rubbone may have been rendered partially insoluble by the gelling action which it undergoes when heated, irrespective of changes arising from vulcanization, but generally it was found possible to extract the unchanged Rubbone at different stages of the process. In the case of Rubbone C it was found that either by limiting the quantities of sulfur or by reducing the time of vulcanization the first effect was to harden the Rubbone to a hard solid with limited thermoplastic qualities similar to hard rubber. After combination had started, a portion only of the Rubbone was combined and the effect of increasing the sulfur content and/or time of vulcanization was first to increase the percentage of sulfur in the combined portion, and when this had reached a maximum to increase the percentage of the maximum product in the

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mixture. Complete conversion was not reached, although it was approached. It will be realized that the study of the vulcanization of the Rubbones presents a simpler problem than the vulcanization of rubber because the Rubbones in contrast to rubber can be separated from the vulcanized products by means of solvents.

Thus A is soluble in paraffins (white spirit). The B fraction is soluble also in acetone, and the C fraction in benzene and alcohol as well. Therefore, the amount of uncombined Rubbone at any stage of the vulcanizing process can be ascertained by extraction with an appropriate solvent such as acetone. The extract will consist of free sulfur and unvulcanized Rubbone, the residue being vulcanized Rubbone. Sulfur estimation on extract and residue will therefore give a complete picture of the constitution of the product.

In the past many attempts have been made to subject vulcanized rubber to a similar operation, but no one has succeeded in extracting unvulcanized rubber from a vulcanizate. If degraded, some rubber may be extracted by solvents such as acetone, but this extracted rubber invariably contains a substantial amount of sulfur combined with it. That is, no separation of raw and vulcanized rubber has taken place, but only a separation into two portions of vulcanized rubber, one of which is more degraded than the other.

There are a number of reagents which have been suggested for producing certain changes, particularly reduced unsaturation regarded as cyclization. One of these is phosphorus trichloride, and in the course of work with this substance its effect in reducing the viscosity of rubber sols has been noted[3].

It has been found that it has the effect of reducing so-called gel rubber to sol rubber, *i.e.*, after treatment the rubber is readily soluble in ether. On the assumption that a part of the vulcanization process consists in the preliminary formation of a special gel form (possibly having elastic qualities), vulcanized rubber after thorough extraction with acetone and ether was swollen in benzene containing phosphorus trichloride and set aside for a few days. Considerable quantities of a soft, sticky material resembling degraded rubber were extracted but, unlike the acetone extract of degraded rubber, the extracted material was without a trace of free sulfur. The expected result was therefore confirmed, and the technique was applied to the vulcanized Rubbones and also to hard rubber. The results from the apparently completed products are appended.

EXPERIMENTAL

The samples of Rubbone in the form of stiff gums were warmed and mixed with sulfur, no accelerator or activator being used. The mixtures, in small tins fitted with lids, were placed in an oven at 150° C. and heated for the times given. The tins were not opened for stirring and this did not seem to be necessary, the final product being apparently homogeneous. After cooling, the products were ground to a powder where possible, or broken into small pieces in the case of the under-vulcanized samples. Since they were honeycombed, plenty of surface was available for extraction. The total sulfur, free sulfur, and combined sulfur were determined in the usual way. The total sulfur was done mainly as a check on the other two. The acetone extract, supplemented by a benzole extract in the case of Rubbone A (this being insoluble in acetone), less the free sulfur, indicated uncombined Rubbone. The extracted residue was dried and weighed and the results were returned in terms of combined sulfur on combined Rubbone = 100.

No.	Total sulfur	Combined sulfur	Free sulfur	Uncombined Rubbone	Combined Rubbone	% combined sulfur on combined Rubbone=100
			Rubbone A. Vulcanized at 150° C. for 8 hours			
1	6.6	6.5	0.1	21.9	71.5	9.1
2	14.9	14.8	0.1	17.9	67.2	22.0
3	17.6	14.6	3.0	14.8	67.6	21.6
4	24.7	20.0	4.7	11.3	64.0	31.3
			Rubbone A. Vulcanized at 150° C. for 24 hours			
5	6.5	6.3	0.2	23.4	70.1	9.0
6	14.2	14.0	0.2	16.8	69.0	20.3
7	21.6	20.4	1.2	13.5	65.5	31.2
8	35.1	21.2	13.9	0.3	64.6	32.8
			Rubbone B. Vulcanized at 150° C. for 8 hours			
9	5.0	4.9	0.1	37.1	57.9	8.5
10	9.8	9.7	0.1	18.3	71.9	13.5
11	20.1	11.6	8.5	11.7	68.2	17.0
12	25.4	12.2	13.2	9.4	65.2	18.8
			Rubbone B. Vulcanized at 150° C. for 24 hours			
13	20.2	14.4	5.8	7.0	72.8	19.8
14	25.4	16.1	9.3	7.3	67.3	24.0
15	30.0	16.9	13.1	0.9	69.1	24.5
			Rubbone C. Vulcanized at 150° C. for 8 hours			
16	6.4	5.1	1.3	38.7	54.9	9.3
17	11.1	9.4	1.7	34.3	54.6	17.5
18	15.8	11.2	4.6	29.4	54.8	22.2
19	17.8	13.1	4.7	24.1	58.1	22.6
			Rubbone C. Vulcanized at 150° C. for 24 hours			
20	6.2	5.6	0.6	23.8	70.0	8.0
21	9.6	9.5	0.1	27.5	62.9	15.3
22	11.6	11.5	0.1	20.9	67.5	17.0
23	15.5	14.4	1.1	20.3	64.2	22.4
24	19.1	16.0	3.1	8.7	72.2	22.2
25	33.6	13.8	19.8	2.0	64.4	21.5

In a more detailed study of the time effect on the vulcanization of Rubbone C, the following results were obtained:

Effect of Time on Vulcanization.

Mixing:	Rubbone C	100
	Sulfur	40

Setting up began after 3 hours at 140° C.

Hours of heating	Total sulfur	Combined sulfur	Free sulfur	Uncombined Rubbone	Combined Rubbone	% combined sulfur on combined Rubbone=100
4	31.6	Nil	31.6	100	Nil	Nil
6	32.8	4.4	28.4	43	24.2	18.2
8	32.5	8.0	24.5	35.3	32.2	24.8

After 3 hours the material was a hard, brittle solid apparently vulcanized. It will be noted that even after 8 hours a considerable amount of uncombined Rubbone remains, although the maximum hitherto obtained was slightly exceeded.

Summary of results. Combined Rubbone=100.

	Maximum combined sulfur
Rubbone A	32.8
" B	24.5
" C	22.6

The calculated figure for rubber on the assumption of one atom of sulfur per isoprene molecule is 47.0. The Rubbone A would therefore appear to be saturated at 70% of this figure and the others at 52% and 48%, respectively.

The iodine absorptions were determined by the Kemp modification of Wijs' method[4] for the three samples of Rubbone with the following results:

Rubbone	A	335 = 90% of value for rubber.
"	B	280 = 75% " " " "
"	C	190 = 51% " " " "

According to various authors, the iodine value of raw rubber corresponds to approximately one double bond per C_5H_8 unit, In that case Rubbone A containing approximately four isoprene units to one oxygen should be 75% unsaturated. Similarly Rubbone B should be 50% unsaturated and Rubbone C saturated as compared with rubber, whereas the actual figures for unsaturation as shown above are appreciably higher.

Again these results are not in conformity with the degree of sulfur saturation, as shown by the maximum combined sulfur figures above.

Putting the various figures together we have the following interpretations to choose from:

Degree of unsaturation taking rubber = 100.

	Theoretical based on oxygen content	Based on combined sulfur	Based on iodine absorption
A	75%	70%	90%
B	50%	52%	75%
C	Nil	48%	51%

No obvious explanation of these variations is forthcoming.

Experiments were conducted with a benzene solution of phosphorus trichloride with a view to extracting any unchanged Rubbone which might have been rendered insoluble by the action of heat alone. Only traces of extractable material were found.

CONCLUSIONS

All three fractions of Rubbone, A, B and C, can be vulcanized by heating with sulfur to yield hard rubber-like products containing, respectively, a maximum of 32.8%, 24.5% and 22.6% of sulfur in combination.

As the unchanged Rubbone in a Rubbone vulcanizate can be extracted with appropriate solvents, the course of the reaction can be followed in greater detail than the vulcanization of rubber.

The theoretical degree of unsaturation of the three fractions, A, B and C, taking rubber = 100, are 75%, 50% and nil. The figures based on combined sulfur are 70%, 52% and 48%, and based on iodine absorption are 90%, 75% and 51%.

This work has been carried out on behalf of the Rubber Producers' Research Association, to whom the authors are indebted for permission to publish this paper.

REFERENCES

[1] Bloomfield and Farmer, *J. Soc. Chem. Ind.* **53**, 43T (1934); Stevens and Stevens, *Trans. Inst. Rubber Ind.* **11**, 182 (1935); Stevens and Popham, *J. Soc. Chem. Ind.* **57** (1938).
[2] *Kolloid-Z.* **8**, 308 (1911).
[3] Communication, referring to cyclized rubber, particularly halide transformations.
[4] *Ind. Eng. Chem.* **19**, 531 (1927).

PREPARATION AND PROPERTIES OF HALOGEN DERIVATIVES OF RUBBER FROM LATEX *

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The rapidly increasing interest which is being taken in the industrial development of halogen derivatives of rubber is shown by the fact that 261 of the 344 patents on the subject abstracted in Marchionna's "Latex and Rubber Derivatives and their Industrial Application", **1937**, have been taken out since 1930. With a few exceptions, these patents refer to the chlorides and hydrochlorides of rubber, bromine and iodine derivatives being of no practical importance, owing principally to the greater cost of manufacture and their lower solubility in organic solvents. Only four of the 261 patents refer to latex, commercial preparation being invariably carried out from a solution of masticated sheet or crepe rubber in an inert solvent. The reaction between rubber and hydrogen chloride does not occur in the presence of appreciable amounts of water, but there is no *a priori* reason why chlorinated rubber should not be prepared directly from latex.

Hopkinson[1] mixed latex with kieselguhr, removed excess water, dried at 200° F., screened the resulting product, and subjected it to chlorine gas. This cannot be considered as a latex process, since at the time of chlorination the rubber must have been in the form of a finely divided dust practically free from water, nor can that of Bradley[2], who chlorinated latex mixed with an organic solvent. Bloomfield and Farmer[3] investigated the action of hypochlorous acid on latex and obtained powders having a chlorine content of 28 to 45%, which could be increased to from 55 to 60% by passing chlorine through an aqueous suspension of hypochlorinated rubber at 80° C. All these materials were yellow powders insoluble in organic solvents. Similar materials containing up to 45% chlorine were obtained when the hypochlorous acid was generated *in situ* (by passing chlorine gas into latex containing excess of sodium bicarbonate), or by the direct chlorination of stabilized acid latex, or of latex containing only small amounts of sodium bicarbonate, carbonate or hydroxide. Bloomfield and Farmer further investigated the effect of temperature, and found that direct chlorination of latex above 50° C. led to coagulation, even in the presence of stabilizers. After the combination of 1 mol. of hypochlorous acid, however, with the equivalent weight of C_5H_8 radical, the chlorination could be completed at 80° to 100° C. Insoluble materials were obtained with one exception, when a white powder was obtained which was readily soluble in many organic solvents. This material was obtained from one batch of latex, all other latices yielding only yellow insoluble substances, and after two months this latex gave insoluble materials. The effect was considered to be due to the catalytic effect of some serum component, since addition of serum to latex sometimes enabled soluble products to be obtained.

The I.G. Farbenindustrie A.-G.[4] have patented the oxidation of latex prior to chlorination in the presence of stabilizers which prevent the coagulation of latex by acids, *e.g.*, ten days' aeration in the presence of an oxidation catalyst. Technically valuable and soluble products are claimed as a result of this treatment,

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chlorine contents of about 50% being obtained. Oxidized latex chlorinated by Bloomfield and Farmer's method (*loc. cit.*) however, produced only insoluble substances unless serum or "skim" was added, but the improvement in solubility obtained thereby was only slight and insufficient to justify the time and labor involved in the oxidation process.

The direct chlorination of latex is also the subject of a patent by the Soc. Chimique du Caoutchouc[5], who chlorinated latex in two stages. In the first stage latex was diluted to 1 to 5% rubber content, and was treated with chlorine in a colloid mill, or was sprayed into a chlorine-filled room, until the chlorine content of the rubber was about 15%. The partially chlorinated material was then allowed to settle, excess water was removed, and the discrete particles were further chlorinated at 80° C. until 40 to 68% chlorine was combined[6].

The preparation of chlorinated rubber from latex has been studied in the laboratories of the London Advisory Committee for Rubber Research with a view to determining not only the type of material obtained when latex is fully chlorinated, but also the effect of small amounts of combined chlorine on the mechanical and physical properties of the rubber, with particular reference to resistance to swelling in oils and organic solvents. The investigation was subsequently extended to a study of the action of bromine on latex.

FULLY CHLORINATED LATEX

When chlorine gas was passed into a sample of latex preserved with formic acid[7] local coagulation occurred, but when the chlorine was developed *in situ* by treating the latex with hydrochloric acid and an oxidizing agent such as potassium permanganate or sodium chlorate no coagulation occurred, the chlorine being taken up rapidly with considerable evolution of heat. In the presence of a considerable excess of chlorine, ranging from 3.84 to 19 atoms per C_5H_8 unit, a pale cream or white powder was obtained, containing about 50% chlorine, which swelled in benzene and chloroform, without however forming a solution. Neither high temperatures (between 50° and 90° C.) nor the presence of chlorination catalysts (*e.g.*, iodine, copper sulfate, ferric chloride, fish glue, serum, carbon tetrachloride or hexamethylenetetramine) effected an improvement in the final products, which contained about 50% chlorine and swelled without dissolving in organic solvents.

Similar products were obtained also from ammonia-preserved latex stabilized with casein, saponin or Aquarex D. When, however, the reaction was allowed to proceed gently so that the temperature did not rise substantially above room-temperature (20° C.) in the initial stages, products of a different type were obtained, readily soluble in acetone, ether, ethyl and butyl and iso-amyl acetates, ethylene glycol monoethyl ether (Cellosolve), benzene, toluene, xylene, chloroform, tetrachloroethane, trichloroethylene, triacetin, dibutyl and diamyl phthalates, ethyl lactate, tricresyl phosphate, benzyl acetate and vegetable oils. They became swollen in carbon disulfide and carbon tetrachloride, and were insoluble in alcohols, cyclohexanone and methyl cyclohexanone and petroleum ether. The method of preparing a soluble chlorinated rubber is illustrated by the following example.

100 ml. of commercial 38 to 40% ammonia-preserved latex were shaken in a 3-liter bolthead flask with 10 ml. of water containing 2 g. of Aquarex D, and acidified with 400 ml. of commercial hydrochloric acid (32%). Sodium chlorate solution (80 g. in 125 ml. water, total volume of solution 155 ml.) was gradually added, slowly at first, to the latex in the flask surrounded by a cold water bath, with mechanical stirring. When the addition of chlorate solution was

completed, *i.e.*, after about 1½ hours, stirring was continued for half an hour and the mixture then allowed to stand for 24 hours at room temperature. The supernatant chlorine water was then decanted and the wet product made just alkaline with dilute caustic soda, filtered, washed thoroughly with water, air-dried two days, and finally kept over calcium chloride in a vacuum desiccator. The resulting white powder contained 51.6% combined chlorine. The quantities of sodium chlorate and hydrochloric acid in the above experiment were sufficient to provide 7.7 atoms of chlorine per C_5H_8 unit, assuming 40 g. of rubber in the latex and that chlorine is liberated according to the equation $NaClO_3+6HCl=NaCl+6Cl+3H_2O$.

EFFECTS OF DIFFERENT VARIABLES

(a) *Latex.*

Contrary to the experience of Bloomfield and Farmer[3], soluble chlorinated rubbers were obtained from all types of latex, which included 40% ammoniated latex from the experimental stations of the Rubber Research Scheme, Ceylon and the Rubber Research Institute, Malaya, as well as both good and off-color latex from other sources, 60% centrifuged latex and triple creamed latex.

(b) *Available Chlorine.*

The following table shows the effect of different amounts of available chlorine on the amount of combined chlorine and the solubility of the product:

TABLE I

Gram-Atoms available chlorine per C_5H_8 unit (*i.e.*, per 68 g. caoutchouc)	% chlorine in product	Characteristics
3.85	37.4	Buff colored insoluble powder
5.77	45.6	White readily soluble powder
7.70	48.4	" " " "
11.55	51.8	" " " "
19.25	55.2	" " " "
38.5	53.8	" " " "

(c) *Temperature.*

In order to obtain readily soluble products, it was found essential to keep the temperature down to atmospheric in the early stages of the reaction. Subsequent heating in an air oven overnight at 50° C. still allowed the formation of a readily soluble product containing 52.9% combined chlorine, but carrying the reaction to its completion in a boiling water bath rendered the resulting material insoluble although it contained 52.5% combined chlorine.

Properties of chlorinated rubbers from latex: Composition.

Analysis of a soluble chlorinated rubber, prepared from latex at room-temperature in the presence of 19.25 atoms of chlorine per C_5H_8 unit, approximately corresponded to the formula $C_{20}H_{26}Cl_{11}O_2$ (required: C 34.85, H 3.78, Cl 56.71%, found C 34.85, H 3.70, Cl 55.8%). The presence of oxygen in these materials seems almost certain and is not surprising in view of the fact that the reaction between sodium chlorate and hydrochloric acid leads to the formation of oxides of chlorine as well as chlorine itself. The chlorinated rubbers obtained

in these experiments are thus different from the insoluble materials obtained by Bloomfield and Farmer by the action of hypochlorous acid on latex which corresponded to C_5H_9OCl, $C_5H_8OCl_2$, $C_5H_7OCl_3$.

TECHNOLOGICAL PROPERTIES

(a) *Stability.*

All the materials tended to develop traces of acidity at room temperature and to discolor and lose chlorine when heated in boiling water. This tendency however diminished with increasing chlorine content, and was only slight in the case of the chlorinated rubbers containing 55% chlorine. Commercial chlorinated rubbers give solutions in xylene[8] which do not discolor at 100° C., and attempts were made to render the present materials stable under these conditions, using 30% solutions in xylene. Chlorinated latex rubbers containing less than 50% chlorine were unsuccessfully treated, but materials containing 52 to 55% were rendered almost completely stable by boiling with 0.01 *N* caustic soda for 15 minutes or stirring a dispersion of chlorinated rubber in 1% sodium carbonate solution at about 60° to 70° C. for six hours. All the materials became black in contact with sulfuric acid at 100° C. The change in color is stated to be characteristic of chlorinated rubbers containing less than 64% combined chlorine[9].

(b) *Solutions for Varnishes and Films.*

Latex chlorinated rubber containing 55% chlorine formed 40% solutions in toluene (40 g./100 ml.) of about 0.25 poise viscosity, which yielded extremely brittle films difficult to detach from glass. Baxter[10] says that 40% solutions of chloro-rubbers in toluene having viscosities of 0.9 poises or less, yield very brittle films, markedly different from those from more viscous solutions. Viscosity is not however a function of chlorine content, for a 40% solution in toluene of a 64 to 67% chloro-rubber may vary from 2 to 22 poises, but depends on the history of the rubber solution prior to chlorination.

PARTIALLY CHLORINATED LATEX

The chlorinated products obtained from preserved latex with smaller amounts of hydrochloric acid and sodium chlorate were examined from the point of view of their vulcanizing and mechanical properties and their resistance to solvents. Details of the preparation of the samples are given in Table II, together with the chlorine contents as found by analysis. For purposes of calculating the quantities of hydrochloric acid and sodium chlorate to add to the latex, the amount of chlorine available was based on the following reaction:

$$NaClO_3 + 6HCl = NaCl + 3H_2O + 3Cl_2$$

Thus one part by weight of sodium chlorate when treated with 2 parts by weight of hydrochloric acid gas (*i.e.*, approximately 5 parts by weight of concentrated hydrochloric acid containing 39.11% hydrochloric acid gas) was assumed to be capable of yielding 2 parts by weight of chlorine. This was termed the "available chlorine" and is expressed as a percentage of the weight of rubber present in the latex (Table II, Column 2). The extent of the reaction is governed by the concentration of the reactants and temperature, as shown by samples 28 to 33f, which were all prepared from latex mixtures containing 30% available chlorine.

The chlorinated rubbers containing less than 5% chlorine were capable of being

creped on the washing mill after first filtering the original crumbly coagulum through muslin and compacting by pressure. More highly chlorinated rubbers were too crumbly to crepe in the usual way, and were dried as granules at room temperature after thorough washing to remove acid, and finally treated in some cases with dilute ammonia.

All the chlorinated rubbers had the serious defect of being very susceptible to atmospheric oxidation. This was evinced by tackiness of the creped rubbers containing less than 5% chlorine, which appeared before the sheets were even dry at room temperature, and by a progressive hardening and "shortening" of the higher chlorinated crumbs. The characteristic smell associated with the oxidation of raw rubber was always present. As the oxidation progressed, the

TABLE II

Serial No.	"Available chlorine," %	Approximate dry rubber content of final mixture	Period of reaction, hours	Maximum temperature, ° C.	Combined chlorine, % of dry rubber
22	20	22	1¼	Room	0.89
28	30	15	2	Shed outside building	1.16[1]
33b	"	"	⅓	45 to 50	1.73[1]
33d	"	12.5	?	40	2.29[2]
33c	"	15	?	Room	3.48[2]
32	"	23	½	"	3.8[3]
24	"	10	2 to 3	About 30	5.31
33f	"	18	3	70 to 80	6.85[4]
23	40	10	2 to 3	About 30	11.56[5]
34	"	15	3	70 to 80	12.4[5]
31	50	14	1 hour at 80		15.0[5]
20	"	17	1½ hours up to 80 to 90° C., 1½ hours cooling		16.14[5]
27	80	12	1 hour up to 80 to 90° C. 1 hour cooling		23.8[5]
21	120	6	2 hours up to 70 to 80° C. cooled by dilution		32.5[5]
25	250	7	70 mins. to about 80° C. cooled by dilution		51.6[5]

[1] Coagulated to a slurry; left overnight.
[2] Set overnight.
[3] Soon coagulated; left overnight.
[4] Chlorate added as crystals to the acidified latex.
[5] All these materials were white powders which settled and could be filtered on a Büchner funnel, washed free of acid, and dried in air. Only sample 25 remained white when dry.

mechanical properties of the vulcanized products deteriorated, and in some cases, notably sample 28, vulcanization appeared to be completely inhibited. This sample, after passing through the tacky stage, eventually became quite brittle and covered with a non-tacky film of a resinous nature. The material stuck badly on the back mixing roll during compounding

Chlorinated rubbers prepared by this process containing 3.8% chlorine and over, as determined by analysis, have been found to be capable of vulcanization without sulfur in the presence of zinc oxide. In the absence of magnesia, the reaction between zinc oxide and the higher chlorinated rubbers at the vulcanizing temperature was so intense as to lead to complete decomposition of the materials with almost explosive violence. Clouds of fumes smelling of burnt pitch were evolved and a tarry liquid remained behind. This decomposition seldom occurred when the chlorinated rubbers were freshly prepared, but the tendency increased with age and the extent of chlorination. With increasing

capacity for vulcanization with zinc oxide, it became more difficult to vulcanize with sulfur and accelerators.

Experiments showed that these chlorinated rubbers had a certain advantage over normal rubber as regards swelling in oils and solvents, but they soon became very weak and could be disintegrated by hand.

Through the cooperation of the Rubber Research Institute of Malaya a set of samples was prepared from fresh field latex in the presence of 25, 30, 40 and 50% available chlorine, both with and without antioxidant in the latex. The chlorine contents were approximately 2, 3, 7 and 12%, respectively; all the samples prepared in the absence of antioxidant were oxidized more or less severely, while of the batch containing antioxidant only the samples containing 2 and 3% combined chlorine seemed to be in good condition. All the samples however were found on examination to suffer from the same disadvantages as those prepared from preserved latex, so that the possibility of obtaining commercially valuable materials by partial chlorination of field latex seems remote.

PARTIALLY BROMINATED LATEX

The modified rubbers obtained by partial bromination of both field and preserved latex showed a marked advantage over partially chlorinated rubbers because they were not easily oxidized and because they dried quickly to strong, non-tacky, fairly stable materials.

Brominated rubbers were prepared from ammonia-preserved latex by a process of which the following is a typical example.

One liter of 38.4% ammonia-latex was treated with 2 g. of saponin dissolved in 20 cc. of water, together with 20 cc. of formalin to neutralize the ammonia. Bromine water (2.5 liters containing 18 cc. of bromine) was added quickly with stirring, and the product allowed to stand overnight. In the morning the material was filtered through filter paper on a Büchner funnel and compacted by hand, when it could be sheeted out on the washing mill. The resulting crepe, which was short and rather dark, was dry after keeping for 48 hours at room temperature. The bromine content by analysis was 9.7%. Experience showed that under similar conditions approximately 75% of the bromine present combined with the rubber.

Samples were prepared containing 6.7, 8.5, 9.7, 12.3, 13.3, 14.7, 16.2, 21.0, 32.3% bromine.

When the Rubber Research Institute, Malaya, attempted to prepare brominated rubbers from field latex by a similar process, difficulty was experienced in coagulating or sedimenting the resulting dilute brominated latex, and it was found necessary to add the bromine to ammonium acetate solution to increase its solubility and reduce the volume of latex after bromination. Antioxidant (Agerite powder) was incorporated with the latex by grinding to a paste with water and shaking vigorously for a few minutes. The dispersion attained probably was not perfect, but it was not desired to add a preservative to the latex in these experiments. After standing overnight the mixture was rolled out through a sheeting battery under a water spray, and soaked for 2 hours in water and air-dried. In the presence of 10, 30, 60 and 80% available bromine, 1.48 5.53, 13.85, 15.17% bromine, respectively, were found in the products. Only 15 to 20% of the bromine in the mixture therefore appeared in the final result. Further samples received from the Rubber Research Institute contained 18.6, 20.5 and 50.7% combined bromine which were brown crepe, black crepe and a brown crumb, respectively.

GENERAL PROPERTIES OF PARTIALLY BROMINATED RUBBER

Mastication and Compounding.

Partially brominated rubbers could be masticated and compounded in the same way as plantation crepe or sheet, absorbed fillers well, but tended to become "shorter" as the amount of combined bromine increased.

Vulcanization.—The behavior of partially brominated rubbers towards vulcanizing ingredients enabled them to be roughly classified into three groups by means of their bromine contents, *viz.*, below 14%; 14 to 30%; over 30%. In the

TABLE III

Mix.—Brominated rubber (9.7% Br) 100; light magnesium carbonate 40, zinc oxide 10, magnesia 5, sulfur 10, tetramethylthiuram disulfide 5 parts by weight.*

Mix.—Standard crepe 100, light magnesium carbonate 40, zinc oxide 10, magnesia 5, sulfur 3, tetramethylthiuram disulfide 1 part by weight.

	Crepe rubber					
			Percentage increase in weight after immersion			
			Petrol (room temperature)		Lubricating oil (100° C.)	
Period of vulcanization at 126° C. (mm.)	Tensile strength (lbs./sq. in.)	Elongation at break (%)	2 days	6 days	2 days	6 days
20	—	—	—	—	—	—
30	950	320	121	129	183	jelly
40	800	295	133	137	126	"
60	740	340	137	141	160	228
			Weak; could easily be pulled apart by hand		Extremely weak	

	Brominated rubber (9.7% Br)					
			Percentage increase in weight after immersion			
			Petrol (room temperature)		Lubricating oil (100° C.)	
Period of vulcanization at 126° C. (min.)	Tensile strength (lbs./sq. in.)	Elongation at break (%)	2 days	6 days	2 days	6 days
20	1280	260	100	118	Small swelling, but surface disintegration, retaining a fair strength	
30	2050	307	77	78		
40	1550	205	72	76		
60	1530	165	65	73		
			Could not be pulled apart by hand; not very resistant to tear			

* It was found in subsequent experiments that the amount of sulfur and accelerator could be reduced to 5 and 3, respectively. Brominated vulcanizates were much tougher than crepe vulcanizates.

first group the rubbery properties were modified in the direction of a greater toughness and decreasing elasticity and tensile strength with increasing bromine content. With the introduction of a small amount of bromine into the rubber went a greatly reduced rate of vulcanization, which however increased with further bromination. Brominated rubbers containing more than 14% bromine were capable of polymerization under heat and pressure in the presence of metallic oxides only (one of which was advisedly magnesia, in order to confer stability during the heating period), although stronger products were obtained when a small percentage of sulfur was present in addition. In one experiment the mix (100 brominated rubber (25% Br), 1 sulfur, 1 zinc oxide, 4 heavy mag-

nesia) was vulcanized for 10 minutes at 148° C. The resulting product was a black, elastic, flexible material having a tensile strength of about 1000 lbs. per sq. in. The third group of partially brominated rubbers was differentiated by the appearance of properties characteristic of moulding powders. Brominated rubber containing 32% bromine was a dark, rather short crepe, which could be changed by heat and pressure into a thermoplastic material, which was hard and brittle when cold.

Action of Oils and Solvents.

Early in the course of this work it was noticed that brominated rubbers were more resistant than normal rubber to swelling by oils and rubber solvents, and as a consequence special attention was paid to the comparison of oil-resisting mixes containing natural and brominated rubber. The samples were weighed before immersion and again after immersion, the surface being washed free from oil with a little petrol and dried with filter paper. The results of the experiments made are given in Tables III, IV and V, which refer to brominated rubber containing about 9% bromine. A characteristic feature of these highly compounded brominated rubber mixes was the extremely tough and hard vulcanizates obtained, which however became flexible when immersed in petrol, lubricating oil and Diesel oil. Experiments were made with brominated rubbers containing larger amounts of bromine, with essentially similar results. The introduction of bromine into the rubber molecule thus has a beneficial effect on swelling in oils and solvents, but its action on other properties such as tensile strength and elasticity after vulcanization is undesirable.

Hard Brominated Rubbers.

The samples of brominated rubber prepared from field latex were compounded to the formula brominated rubber 70, sulfur 30, magnesia 3.5 parts by weight, and vulcanized for periods of 1, 2 and 3 hours at 155° C. a control mix of the same formula from standard crepe being given the same vulcanizing treatment. The types of products obtained are given in Table VI.

Comparative tests on tensile strength, impact strength and plastic yield were made, the results of which are given in Table VII and Figure 1. The tensile strength tests were made on Schopper rings of approximately 1 mm. thickness. As however increased bromine content caused progressive brittleness of the resulting hard rubbers, this test was not very accurate owing to the degree of twist which occurred as the rings were stretched. It is unlikely however that the tensile strength of hard brominated rubber is as great as that of normal hard rubber, in view of the corresponding smaller strength of soft vulcanized brominated rubber when compared with standard crepe. Impact strength was measured on a modified Charpy pendulum machine. The dimensions of the test-pieces used were 50×5×5 mm., the supports were 32 mm. apart, and the striking edge of the pendulum was of $\frac{1}{16}$ in. radius. The plastic yield curves were obtained with a Hutchinson apparatus for measuring the twist of bitumen, with the grips suitably modified to take the test-piece, whose effective dimensions were 54×11×5 mm. The torsional stress on each sample was 150 g. cm.

The results of these comparative tests indicate that hard brominated rubber containing 15 to 20% bromine is definitely more brittle but softens less with temperature than normal hard rubber, and suggest that bromination to a smaller extent than 15% may give a useful hard rubber having a higher plastic yield point than normal, but with reduced tensile strength and increased brittleness.

TABLE IV

Mix—Crepe rubber 100, carbon black 40, zinc oxide 10, magnesia 5, sulfur 3, tetramethylthiuram disulfide 1.5, phenyl-β-naphthylamine 2, cotton seed oil 4 parts by weight.

Mix.—Brominated rubber (9.7% Br) 100, carbon black 40, zinc oxide 10, magnesia 5, sulfur 10, tetramethylthiuram disulfide 5, phenyl-β-naphthylamine 2, cotton seed oil 4 parts by weight.

	Crepe rubber				Brominated rubber (9.7% Br)			
Period of vulcanization at 126° C. (mm.)	Tensile strength (lbs./sq. in.)	Elongation at break (%)	% increase in weight after immersion in petrol (room temperature) 1 day	5 days	Tensile strength (lbs/sq. in.)	Elongation at break (%)	% increase in weight after immersion in petrol (room temperature) 1 day	5 days
30	2210	447	107	118	1580	214	58	68
40	2050	420	103	111	860	45	45	50
60	1670	378	105	113	910	50	45	50

Mix.—Neoprene 100, carbon black 40, zinc oxide 10, magnesia 10, sulfur 1, phenyl-β-naphthylamine 2, cotton seed oil 3.

	Neoprene			
Period of vulcanization at 141° C. (min.)	Tensile strength (lbs./sq. in.)	Elongation at break (%)	% increase in weight after immersion in petrol (room temperature) 1 day	5 days
40	2130	585	16	23
60	2430	518	14	25
80	2120	421	14	25

TABLE V

Mix.—Crepe rubber (100 volumes) 93, zinc oxide 10, magnesia 5, P 33 gas black (50 volumes) 90, sulfur 2.5, tetramethylthiuram disulfide 1.5, phenyl-β-naphthylamine 2 parts by weight.

Mix.—Brominated rubber (8.5% Br, 100 volumes) 100, zinc oxide 10, magnesia 5, P 33 gas black 90, sulfur 5, tetramethylthiuram disulfide 3, phenly-β-naphthylamine 2 parts by weight.

Period of vulcanization 60 minutes at 126° C. Vulcanizates immersed in Diesel oil at 55° C. for stated periods[11]. Tensile strengths were determined on the Schopper ring testing machine immediately after removal from the oil and calculated on the cross-section of the swollen rings.

Sample	Tensile strength (lbs./sq. in.) after 0	2	4	6 days	% increase in weight after 0	2	4	6 days
Crepe rubber	1550	170	160	180	—	68.2	84.2	95.0
Brominated rubber (8.5% Br)	1350	440	470	405	—	48.7	58.7	64.7

TABLE VI

Bromine content of sample	Types of material obtained after vulcanization at 155° C. for periods of 1 hour	2 hours	3 hours
nil	Nearly hard rubber	Hard rubber	Hard rubber
1.58	Soft vulcanized rubber	Nearly hard rubber	Just hard rubber
5.53	Harder than preceding	Nearly hard rubber	Hard rubber
13.85	" " "	Hard rubber	" "
15.17	" " "	" "	" "
18.6	Harder than preceding and nearly hard rubber	" "	" "
20.5	Nearly hard rubber	" "	" "

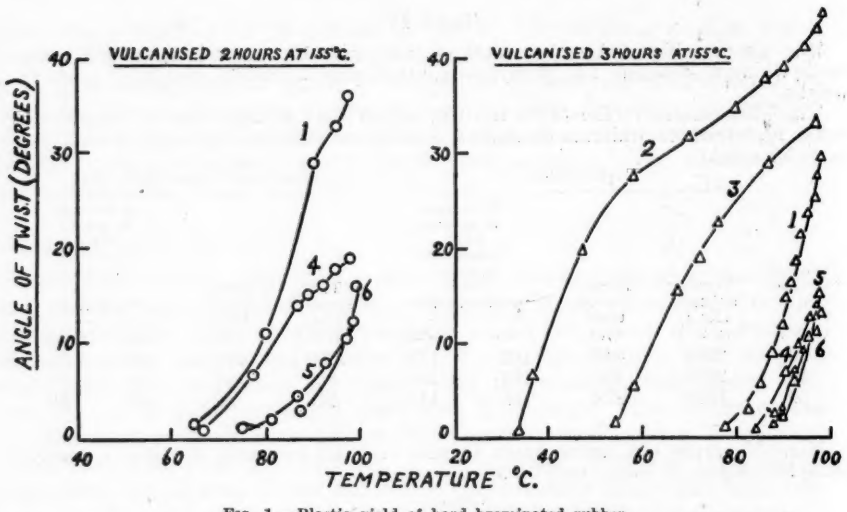

FIG. 1.—Plastic yield of hard brominated rubber.
(Torsional Stress 150 g.-cm.). Effective Dimensions of Test-Pieces 54 × 11 × 5 mm.

1. Control.
2. 1.58% Bromine.
3. 5.53% Bromine.
4. 15.17% Bromine.
5. 18.6% Bromine.
6. 20.5% Bromine.

TABLE VII

Bromine content of rubber	Properties of hard rubber after vulcanization for periods of 2 and 3 hours at 155° C.			
	Tensile strength (lbs./sq. in.)		Impact strength (ft. lb.)	
	2	3	2	3
nil	4420	5260	0.60	0.92
1.58	soft	2840	too soft to break	
5.53	soft	3600	—	0.63
15.17	2960	3540	0.18	0.09
18.6	brittle	brittle	0.04	0.06
20.5	"	"	0.05	0.06

SUMMARY AND CONCLUSIONS

The paper deals with the preparation and properties of chlorine and bromine derivatives of rubber from latex, obtained by the generation of nascent chlorine *in situ* and by the addition of bromine water. Attention was given to compounds containing small amounts of halogen, which still showed marked elasticity, in addition to the powders containing large proportions of halogen.

When stabilized preserved latex was treated with an excess of hydrochloric acid and a suitable amount of oxidizing agent, an exothermic reaction occurred which, if uncontrolled, led to the formation of white powders containing about 50% chlorine which swelled in organic solvents without dissolving. If, however, the temperature was not allowed to rise substantially above atmospheric, at least in the early stages of the reaction, products of similar appearance and chlorine content were obtained, which nevertheless were readily soluble in a wide range of solvents, including vegetable oils, to give thin solutions which formed brittle films adhering strongly to glass and metal. Analysis of a chlorinated rubber containing 55.8% chlorine corresponded approximately to the formula $C_{20}H_{26}Cl_{11}O_2$.

Partially halogenated rubbers prepared from both field and preserved latex by the processes mentioned were examined for their behavior towards vulcanizing ingredients and the physical properties of their vulcanizates. Chlorinated rubbers readily perished in air at atmospheric temperature, but brominated rubbers were considerably more stable. The introduction of a small amount of halogen into the molecule caused a marked retardation in rate of vulcanization of the resulting halogenated rubber, which however, increased with further combination of halogen. There appeared to be a gradual decrease in tensile strength and elasticity with increasing halogenation, accompanied by reduced swelling in oils and solvents. After a certain proportion of halogen had combined, *viz.*, about 4% chlorine or 13% bromine, vulcanization occurred in the presence of metallic oxides, although stronger products were obtained with the addition of a small percentage of sulfur. The hard rubber reaction was retarded by the introduction of a little halogen, but further combination gave products which were faster vulcanizing than normal rubber. The resulting hard rubbers were brittle, but possessed a higher plastic yield point than hard rubber from standard crepe. Thermoplasticity was observed in partially halogenated rubbers containing more than approximately 15% chlorine or 30% bromine.

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REFERENCES

[1] *U. S. Patent* 1,491,265 (1923).
[2] *U. S. Patent* 1,627,725 (1927).
[3] *J. Soc. Chem. Ind.* **53**, 43T (1934).
[4] *British Patent* 390,097 (1933).
[5] *French Patent* 793,607 (1936).
[6] Nielsen, "Chlorkautschuk", Leipzig, **1937** p. 22.
[7] Rhodes and Sekar, *J. Rubber Res. Inst. Malaya* **7**, 179 (1937).
[8] Anon., *India-Rubber J.* **88**, 15 (1934).
[9] Nielsen, *Paint Manuf.* **6**, 153 (1935).
[10] *J. Soc. Chem. Ind.* **55**, 407 (1936).
[11] Naunton, Jones and Smith, *Trans. Inst. Rubber Ind.* **9**, 169 (1933).

CYCLIZED RUBBER, PARTICULARLY HALIDE TRANSFORMATIONS *

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INTRODUCTION

Rubber can be modified in a number of ways. The type of modification with which it is proposed to deal is known as "cyclization." The alteration in the properties of rubber so brought about is generally explained on the assumption that the double bonds of the C_5H_8 units in the rubber molecule are caused to link by bridging, thus forming isomers which are less unsaturated than the original rubber.

The unsaturation of the modified rubber compared with the original rubber is therefore an important factor in assessing the degree of cyclization which has taken place.

These compounds can be formulated from the rubber molecule by assuming an intermediate additive compound with the reagent. In some cases, as in the reaction with $SnCl_4$, such compounds have been isolated.

Nearly all known methods of cyclization are believed to give rise to polycyclo rubbers in which there are assumed to be four C_5H_8 units per double bond compared with two in the case of the mono type and one for rubber. As a result the degree of unsaturation should be only 25% of that of the original rubber. A monocyclo rubber, such as is said to be obtained from the HCl-addition product, should have a 50% degree of unsaturation.

Cyclized rubbers differ from ordinary rubber according to the extent to which they have been treated. They have been described as ranging from comparatively soft materials, through stages reminiscent of gutta-percha and hard balata, to the final stage which may be a whitish amorphous powder, a tough fibrous or horny insoluble material, or a very brittle shellac-like substance. In some cases the intermediate stages are not always realizable.

It is not proposed to discuss the theories of macromolecular structure which have been put forward to explain the changes in the physical properties of the cyclized products or the viscosity of the solutions. Reference may be made to Staudinger and Schulz[1] and others. Attention may be drawn also to the paper by Thies and Clifford[2] in which the various types of chemically modified rubber are reviewed as a preliminary to a description of Plioform. In reference to the present work it is, however, necessary to discuss briefly those reactions which are believed to result in cyclized products.

There are a number of reagents which will bring about the cyclization of rubber, as evidenced by the fact that the properties of the rubber are changed without alteration of the empirical formula and with production of a less unsaturated derivative. These are detailed below. Incidentally, it is possible that some reagents that react with the rubber molecule simultaneously convert a part of the rubber to a cyclized state which may then itself react. The present review does not deal with reaction products of rubber containing foreign elements such as chlorine, whether cyclized or not.

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Cyclization may be brought about either by milling the reagent into the rubber on ordinary mixing rollers or by allowing the reagent to react on a rubber sol in a suitable medium. The first method is economically the more desirable as more direct, but it is not suitable for all reagents. The reaction in presence of a solvent is generally uniform and regular, as a complete mixture of the reagent and the rubber is rapidly attained. So far as can be judged from the literature, very different products are obtained according to the method that is chosen.

The reagents which have been used are as follows:—

I. *Sulfuric Acid*[3], *Sulfonic Acids and Sulfonic Chlorides*[4].

(*a*) These reagents when milled into rubber and subsequently heated in the form of sheets give rise to tough thermoplastic materials said to resemble gutta-percha or balata. But on the other hand, if heated in bulk, a shellac-like thermoplastic is produced, owing to the reaction being exothermic and a consequent higher temperature of reaction. On account of the fact that the degree of unsaturation (55 to 65% of that of rubber) of these materials does not conform to that of polycyclo rubbers which are theoretically of the order of 25%, they have been given the general name of Thermoprenes. They are more or less soluble in the usual rubber solvents and can be vulcanized. They are useful for bonding rubber to metal. These products[5] have been described in considerable detail by Fisher[4], also by Fisher and McColm[6]. It is stated that three types of substances may be obtained according to the intensity of the reaction as governed by the nature and amount of reagent, and by the temperature and duration of the reaction. They are somewhat as follows:—

(1) Resilient or elastic substances similar to vulcanized rubber.
(2) Hard tough heat plastics variously resembling balata, hard balata, and gutta.
(3) Hard, tough or sometimes brittle and friable, products resembling shellac.

Little or no information is supplied as regards (1), while (2) covers a variety of products of varying degrees of hardness, denoted by the letters GP resembling gutta-percha and HB hard balata. Products under (3) are labelled SL for shellac.

These descriptions referring to the physical state are not altogether satisfactory, as gutta-percha and balata vary considerably according to grade and provenance. The properties of the natural hydrocarbons are considerably modified by the nature and amount of accompanying resins. Also, the hydrocarbons themselves are very tough, horny materials, although retaining thermoplastic properties. Presumably, HB is a harder product than GP, but from a table describing the physical properties it appears that a sample B described as an HB type is intermediate between sample A described as a GP type and samples C and D which are of the HB type. A notable feature of all these products is the relatively high temperature employed in their preparation and relatively long period of heating as, for example, 6 hours at 141° C. (sample A) and 24 hours at 120° to 125° C. (sample C). In the preparation of the SL type the temperature is still higher owing to the exothermic nature of the reaction.

The SL type can be purified to give a white powder; the others are more difficult to free from coloring matter.

It is notable that all types can be vulcanized, yielding "non-thermoplastic products like hard rubber." Hard rubber is, however, to some extent thermoplastic so that this statement requires modification.

The products are less unsaturated than rubber to the extent of 55 to 65%, judged by the maximum combined sulfur content or by the Kemp-Wijs method. The chemical unsaturation of a GP product was found to be 65%, while that of the SL type is 57. This would be expected if the intensity of the reaction for the GP is less than for the HB or SL types, although no figures are given for the chemical unsaturation of the former. The analyses approximate to the C_5H_8 ratio but do not exclude the possibility of presence of some oxygen. The authors state that in general aspects the reaction is much like ordinary vulcanization with sulfur and draw appropriate conclusions.

(*b*) A process[7] has been described whereby rubber is first liquefied, that is to say, converted to molten rubber, and subsequently treated with sulfuric acid, sulfonic acids, their chlorides or esters, pyridine, sulfuric anhydride, or metal halides, with or without the addition of phenolic substances. The products are thermoplastic, and may be black or brown, tough and slightly elastic or brittle.

Rubber liquefied by heat, that is, so-called molten rubber, is profoundly altered and regarded by some as cyclized. The products appear to resemble the SL type, that is, the result of intensified reaction.

(*c*) The reagent may be added to concentrated latex[8]. Thus treatment of latex with sodium silicate and acetic acid is followed by the addition of the sulfonic acid. After this the whole is taken to dryness and heated.

This seems to be an alternative method of mixing in the reagents.

(*d*) Dialkyl sulfates[9] are heated with benzene solutions of rubber for several hours, with subsequent evaporation of the solvent. Further heating, *e.g.*, at 125° C. for 21 hours, gives thermoplastic materials.

This again appears to be no more than a variant of the earlier procedure.

II. *Amphoteric Halides.*

When such halides are milled into rubber and the products heated, an exothermic reaction takes place and hard thermoplastic products are formed[10].

The iodides are the most active, the chlorides the least. The fluorides are excluded as being inactive. The products vary in toughness and hardness according to conditions of treatment. The product from ferric chloride is black, those from the chlorides of aluminum, tin and bismuth are light colored.

In place of milling the reagent into rubber it may be added to a solution. Chlorides of iron, antimony, titanium and tin may be used. They form a complex with the rubber which can be split off by treatment with alcohol, leaving a cyclo rubber. The reaction in benzene requires 24 hours at 80° C. Carried to completion the product obtained with stannic chloride is a white powder, separable into a benzene-soluble and an insoluble fraction in the proportions of 3: 1. The soluble polymer is also a fine white powder softening at about 220° C., which oxidizes spontaneously in air, increasing in weight by 12%. It yields mobile solutions with rubber solvents, but is soluble only with difficulty in ether. It is insoluble in alcohol or acetone. The insoluble polymer is white, fibrous and inelastic, and oxidizes only very slowly[10]. But according to a patent[20], the benzene-soluble polymer is obtained by carrying out the reaction in an inert atmosphere. If not, a portion of the product consists of powdery insoluble oxides of the polymer. The reaction is complete in 24 hours at room temperature, or in a much shorter time if heated. The insoluble polymer is peptized in solution by the soluble but can be separated by frequent extractions. Both absorb oxygen from the air to produce white powdery oxides. The degree of unsaturation of both products is stated to be less than that of rubber.

III. *Halogenated Stannous and Stannic Acids.*

Thermoplastic products ranging from a tough balata-like to a hard-rubber consistency are produced by milling rubber with chloro- or bromostannous acid, with or without subsequent heating to 130° to 150° C.[11]

The action of these acids on rubber either by milling or in solution is the basis of the Plioform type of resin[12]. The products contain a variable proportion of bound chlorine. They vary in hardness and range from balata-like to hard rubber-like materials. They are soluble in the usual rubber solvents and are said to be acid- and alkali-resistant. They have a low water absorption. The softening point of this type lies between 79° and 107° C. Full details are given of the physical properties of the standard types, but little data can be found dealing with the range of products or the differences resulting from carrying out the reaction in solution instead of on the mill.

IV. *Organic Acids, their Chlorides and Anhydrides, with or without Additions.*

(*a*) The action of trichloroacetic acid in producing a rapid reduction of the viscosity of rubber sols is well known. This acid with or without phenols, incorporated in rubber either in solution or by mastication with subsequent heating for long periods, gives hard tough thermoplastics[13].

(*b*) Rubber solutions treated with acid anhydrides, *e.g.*, acetic, propionic or chloracetic, with small quantities of chloroacetylsulfuric acid or thioacetic acid, give balata- or shellac-like materials which are thermoplastic. On long heating they become brittle[14].

(*c*) Products whose resistance to attrition is said to be due to their "strongly interlaced cyclic net-like structure," are obtained by the action on rubber solutions of mixtures of preferably acidic catalysts[15] such as:—

Tin tetrachloride and organic acid chlorides.
Aluminum chloride and organic acid chlorides or phosgene.
Zinc chloride and alcohol or acetic anhydride.

The authors suggest that conversion is due to the formation of organo-inorganic oxonium compounds.

V. *Non-metallic Halides and Oxyhalides.*

Under this heading are included the halides and oxyhalides of phosphorus and boron inclusive of their reaction products, such as hydrofluoboric and fluoboric acids.

(*a*) Thermoplastic materials of various characteristics, soft and extensible, gutta-percha-like and brittle, are obtained by the action of phosphorus oxybromide alone, or mixed with the oxychloride or trichloride, on rubber solutions at ordinary or elevated temperatures[16]. They can be vulcanized.

A rather unusual variation of this process[17] consists in the use of a reagent containing a higher proportion of oxygen than that in $POCl_3$. Treatment is carried out in solution at the ordinary or elevated temperature and is said to be accelerated by ultraviolet radiation. The products are relatively hard at ordinary temperatures, but soften at 100° C. They may be chlorinated without the difficulties which normally attend the chlorination of rubber.

The use of fluorides of phosphorus in the presence of a dehydrating agent has also been suggested[18].

A thermoplastic material is obtained by milling into rubber a substance which will liberate water, *e.g.*, crystalline aluminum sulfate. A material which will react with water to form acids, *e.g.*, phosphorus pentachloride, is subsequently incorporated and the whole heated at 160° C.[19]

(*b*) Boron trichloride as "a halide salt containing residual affinity" in common with a number of similar metallic halides is said to convert rubber in an inert atmosphere into a white powder soluble in benzene[20]. On melting, the material becomes shellac-like, and in air it oxidizes to an insoluble material.

(*c*) Several patents record the use of boron trifluoride, notably for toughening rubber surfaces[21], while another[22] refers to the use of a product obtained by treating rubber solution with this reagent and cresol. Other claims are for boron trifluoride used in the presence of a dehydrating agent[18] and for hydrofluoboric and fluoboric acids, and also benzenediazonium fluoborate, which on heating evolve boron trifluoride[23].

(*d*) A process[24] consisting essentially in heating rubber (with or without a solvent) in a closed vessel at 150° to 300° C. for 20 hours in the presence of a porous surface-acting substance of slightly acid reaction, preferably an active carbon or bleaching earth, is said to give transparent resinous materials of brownish color, softening at 50° C. They are still unsaturated and can be hydrogenated to colorless resins.

(*e*) Under the influence of high tension alternating currents, oxygen being rigidly excluded, a yellowish powder was obtained by Fromandi[25] from purified rubber after 8 hours' exposure. The degree of unsaturation corresponds to the disappearance of about two-thirds of the double bonds, and in other respects the material has the characteristics of a cyclized rubber.

EXPERIMENTAL

The present investigation has been concerned with a rubber cyclized in solution by means of boron trifluoride or materials which give rise thereto. It will be noted from the foregoing short review that there are no publications dealing with the action of this reagent or the products obtained with it except patent specifications and these are not a satisfactory source of information. Consequently an independent investigation was desirable. The reaction has been tried by adding the reagents directly to rubber on the mill, but control is difficult and the results are unsatisfactory.

By treating rubber in a pure solvent with boron trifluoride, soluble products ranging in a continuous manner from a soft rubbery to tough leathery consistency can be obtained. The end product is a shellac-like material. This range suggests that these products are merely degrees of the same conversion, which can be varied by the conditions of the reaction. An insoluble isomer has also been obtained.

Practical rather than theoretical considerations gave rise to the investigation, the chief object in view having been the production of a material of specific properties, notably that of alkali-resistance, as a basis for paints, *i.e.*, as a medium or binder.

It has been found that this material is a "breather," unlike chlorinated rubber, Neoprene, coumarone resin, and Pliofilm which are "sealers." That is to say, it will allow the passage of aqueous solutions. When used as a binder for paint in lieu of oil, this still holds good with the added advantage that the pigment is protected even when the aqueous solution is alkaline or acid. This effect may be demonstrated in a striking manner by means of Prussian blue, which is

very sensitive to alkali. Two paints containing Prussian blue, (A) made with oil, (B) made with the cyclized rubber, are each painted on one-half of a freshly made concrete block. Half of each is now over-painted with A and the block stood in a little water or the underside kept wet. It will be found that whereas the single and double coats of A will be entirely discolored and the pigment destroyed, B alone will be unaffected. Also, the over-coat of A on B will be gradually destroyed by the alkali permeating through B, although having no effect on the pigment incorporated in B.

Degrees of Conversion most Desirable.—It has been found that there is an optimum degree of conversion which provides the most suitable material for our purpose. In this state the conversion is apparently fairly advanced and lies between the rubbery and brittle stages. A typical product is fairly tough, has little or no elasticity, is transparent in thin layers, will stand a considerable amount of flexing, and as a varnish brushes well and forms very hard but not brittle films, with very good adhesion. Easily soluble in the ordinary rubber solvents, it can be manufactured in white spirit at concentrations up to 40 to 50%, and as such can be used directly as a binder for incorporation in paint.

The chief factors which influence the degree of conversion are the (1) Proportion of reagent, (2) temperature, (3) solvent, (4) concentration and viscosity, (5) duration of reaction.

Reagent.—Since boron trifluoride is a gas at normal temperatures and the liquid has a b.p. of 101° C., it is not, *per se*, a satisfactory reagent. There is also the difficulty of assuring the absorption of the correct proportion. Moreover, since it is insoluble in the solvents used, most of it is lost if bubbled through the reaction mixture. Boron trifluoride may, however, be dissolved with the aid of substances such as pyridine, alcohols, ethers and acids. The products are not mere mixtures but definite compounds[26], *e.g.*, $C_5H_5N.BF_3$ is crystalline, m.p. 45° C., while $(CH_3COOH)_2.BF_3$ appears to be an acid of approximately the same strength as hydrochloric acid, judged by its electrical conductivity. In our practice, the reagent is made by passing boron trifluoride into glacial acetic acid and noting the increase in weight. It is convenient to adjust this to a 50% concentration. The excess of acetic acid probably acts as a dehydrating agent. Other boron trifluoride derivatives which have been used for the reaction are fluoboric acids and mixtures of boric and hydrofluoric acid.

The proportion of boron trifluoride required is small; it varies from 2 to 3½% according to conditions, *i.e.*, rubber concentration, boiling point of solvent and viscosity of solution. In the case of fluoboric acid, 7 to 8% is needed.

Duration of Reaction.—For small batches using boron trifluoride, about ¼ hour is required, but, with larger quantities and greater concentrations, a longer period of treatment is necessary. Using fluoboric acid, 2 to 3 hours are required.

Rubber.—Generally speaking all types of raw rubber can be used, including smoked sheet, crepe, also dialyzed and whole dried latex.

Solvents.—In our earlier experiments reactions were carried out in pure benzene or carbon tetrachloride, at the boiling point. It was found that commercial benzene, toluene and xylene contained unsaturated components which are very reactive towards BF_3, resulting in the production of oils. These oils have a plasticizing action, and therefore made it difficult to determine the degree of conversion by an examination of the product. They also reduced the effective concentration of reagent, resulting in the rubber being insufficiently converted. As a major end in view was the incorporation of this material in paint, it was considered advisable to use, if possible, a normal paint thinner as solvent. White spirit, a petroleum fraction which is extensively used as a turpentine

substitute, was found to vary considerably in its reactivity to BF_3. However, both good and bad samples responded to agitation at 100° C. with concentrated H_2SO_4 and subsequent treatment with lime. The solvent purified in this way yielded only traces of oil with BF_3 and could be used without further treatment. If the white spirit contains very large quantities of unsaturated substances, it may be necessary to redistil it to obtain a suitable product. The white spirit used had a boiling range of approximately 150° to 190° C.

Solution.—Ordinarily dilute solutions of milled rubber were made in the ususal way, but those of high concentration necessitated special measures to reduce their viscosity. This is best accomplished by disaggregating the rubber by prolonged milling or heating, or by the use of softeners such as cobalt linoleate, phenylhydrazine, or phosphorus halides or oxyhalides. Small proportions were milled into rubber or placed in the solvent, and the rubber was allowed to swell. By this means concentrations up to 50% may be prepared.

Several patents claim the production of thermoplastic cyclorubbers by means of halides and oxyhalides of phosphorus. With quantities of about 1%, disaggregation but no cyclization appears to occur, as there is no change in the degree of unsaturation. The viscosity reduction with these reagents is spectacular.

The Reaction.—The solution is heated to the required temperature and the reagent is gradually mixed in with efficient stirring. A reddish coloration appears, which eventually becomes brownish, its intensity depending chiefly on the type of rubber used. The addition of the acetic acid-boron trifluoride reagent effects a gradual lowering of viscosity which runs approximately parallel with the course of the reaction. Using fluoboric acid with white spirit as a solvent at 130° to 140° C., there is a slight initial fall in viscosity followed by a very marked thickening, as if the mass were gelling. Thereafter a reduction of viscosity gradually occurs. This is reminiscent of the action of chlorine on a rubber sol.

To determine when the desired degree of conversion has been achieved is a matter of experience under any particular set of conditions, but in general it may be said that, with the appropriate concentration of the reagent, this is attained when there is no further fall in viscosity, the mix being watery in consistency and having entirely lost the characteristics of a rubber sol. It is advisable to determine the minimum reagent necessary for a particular set of conditions, and it is then found that if the treatment is unduly prolonged, conversion to the final brittle stage does not occur, but the product may be slightly inferior in its adhesive power.

Temperature of Reaction.—With benzene, toluene and carbon tetrachloride as solvents, the reaction is carried out at the boiling point with gentle refluxing, but when using white spirit a temperature of 130° to 140° C. is necessary. It is possible, but not practicable, to carry out the reaction in the cold. Some days are required for completion and there is also a great tendency towards the production of the insoluble isomer discussed later.

Isolation of Product.—When the material is required in solution, as for the manufacture of paint, neutralization is effected by means of substantially anhydrous sodium carbonate, which is first made to a slurry with a little of the reaction product and then stirred into the hot bulk. Settling of suspended matter is facilitated by keeping the mixture warm.

In the earlier experiments sodium carbonate solution was used for neutralization, but the subsequent treatment, entailing heating in the moist state, converted the material partially or wholly into an insoluble oxidation product. Gaseous ammonia may also be used. It has the advantage of not introducing any excess material over that actually required for neutralization.

If solid material is required, evaporation at low temperature *in vacuo* may be employed, or it may be precipitated by stirring into a large bulk of miscible non-solvent such as alcohol or acetone.

Utilization in Paints.—The solution in white spirit is used direct; there is no need to recover the material free from solvent when using white spirit as the medium in which the reaction is carried out.

No trouble was experienced in making paints using a variety of pigments which could be applied to surfaces in a normal manner. When dry these usually had a slight gloss. They aged satisfactorily. Weathering tests carried out on these paints incorporating lithopone, white lead, or zinc oxide-titanium oxide mixture as pigments showed that the cyclized rubber behaved similarly to oil as a binder.

Properties of Conversion Product.—The properties of the product depend on the degree of conversion. When somewhat underconverted, it is soft and weak and breaks when a strip is stretched two or three times its original length. It shows very pronounced hysteresis. A piece stretched to four or five times its original length, just short of breaking, curls on itself and does not contract appreciably until warmed, when it rapidly unrolls and recovers almost completely. With fuller conversion it becomes harder and stiffer and of a leathery character. It is thermoplastic in that it softens at about 120° C. It never becomes as plastic as rubber.

It adheres strongly to glass, porcelain and metals, when evaporated to give a film.

It can be vulcanized. A mixture consisting of conversion product 100, sulfur 4, zinc oxide 5, and accelerator (piperidium pentamethylenedithiocarbamate) 1, heated for 16 hours at 70° C., yielded a material resembling the original conversion product when handled, but which was rather stiffer and when stretched recovered almost completely without requiring to be heated. It behaved substantially like a "pure" vulcanized rubber except that it was leathery to the feel and weaker. The effect of vulcanization on the conversion product is therefore similar to that on raw rubber but modified in accordance with the effect of the conversion.

The following mix was vulcanized at 100° C. for 336 hours, the combined sulfur being unchanged from that after 168 hours:

Cyclized rubber	100 parts
Sulfur	75 "
Zinc oxide	20 "
Zinc diethyldithiocarbamate	5 "

A similar mix using crepe was treated for comparison. After acetone extraction and treatment with ether-HCl (for the removal of sulfur in the form of zinc sulfide), sulfur determinations were made. After allowance for zinc oxide present, the results were:

Combined sulfur per 100 parts cyclized rubber	54.2
Combined sulfur per 100 parts rubber[37]	61.3

It is evident that a portion only of the sulfur in each case is additive at the double bonds, and the results are in conformity with the reduced unsaturation coincident with cyclization.

The vulcanizates were brown, the cyclized sample being the lighter. It was the more brittle and softened more easily than the rubber sample in boiling water.

A most interesting fact emerged during these vulcanizations. One series had been heated between glass plates. The ordinary hard rubber separated quite easily, but in the case of the cyclized material it was absolutely impossible to remove it from the glass, so firmly did it adhere. The use of force merely caused the glass surface to flake or splinter.

Cyclized rubber obtained with BF_3 is pale to brownish, transparent or translucent in thin films. The color of the finished product is governed by that of the starting material, pale milled crepe giving a substantially colorless film.

It is soluble in ordinary rubber solvents, but insoluble in alcohol and acetone, thus resembling raw rubber in solubility.

It can be incorporated with coumarone resin, paraffins, ester gum, rosin, chlorinated naphthalene and mineral oils. Ester gum, rosin and coumarone resin harden it; mixed with 50% of the latter, it forms a good tough film.

The inflammability is less than that of rubber and decreases with increased conversion.

Alkali resistance has been found to be of a high order, the material being a "breather" not a "sealer." It is an effective pigment protector.

Degree of Unsaturation.—The degree of unsaturation decreases with increased conversion. Using a modification of the Kemp-Wijs method the following figures were obtained:

	Iodine number
Milled crepe	354
Milled crepe disaggregated by PCl_3	353
Cyclized rubber (normal product)	220
Cyclized rubber (fully-converted)	193

According to theory, complete cyclization should reduce the unsaturation to one-quarter of that of the original rubber (see particularly the work of Staudinger[1]). It is obvious from the figures obtained on vulcanization and iodization that unsaturation is reduced to a far less extent. The vulcanization was carried out at a very low temperature, *viz.*, 100° C., precluding pyrogenetic changes. Yet the degree of unsaturation was 88% of that of the original rubber similarly treated. The iodine figure, which is perhaps the more reliable, gave the corresponding figures of 62% for the normal product and 55% for the fully converted product. Thus, in the latter case unsaturation is still double that of a completely cyclized rubber. If the iodine figures are preferred to the sulfur figures then the vulcanized BF_3 conversion product must contain a much larger proportion of substituted sulfur than does ordinary hard rubber.

An analysis was made of the conversion product purified by solution in carbon tetrachloride and precipitation with acetone three times. This gave as an average of two reasonably close determinations, C=83.66%, H=11.47%. The residue, presumably oxygen, after deducting the value of a trace of ash, was 4.87%. How far this oxygen is a normal constituent of the conversion product is open to question on account of the difficulties attendant on purification, although pains were taken to restrict access of oxygen during purification. It appears in any case that the C_5H_8 complex has lost a part of its hydrogen.

Oxidation of the Material.—Two different oxidation products are formed according to the method used. It has been observed that thin films become brittle after a lapse of time. As this can be largely prevented by antioxidants, the process would seem to be one of oxidation. This reaction has not yet been fully investigated.

The first oxidation product, a brittle insoluble material similar in all respects to the aged film, has been obtained from the conversion product:

(*a*) By air oxidation, *i.e.*, blowing at 70° C. a solution in white spirit, using cobalt linoleate as catalyst. Oxidation does not occur readily without a catalyst. The oxidation product being insoluble is thrown out in gel form.

(*b*) By steam distilling or heat drying the moist conversion product (*vide infra*) a white insoluble material is also obtained.

(*c*) By oxidation, as by shaking a solution with potassium permanganate and acetic acid. In this case also the material is thrown out as a gel, which dries to a white insoluble product.

Details of Aged (Oxidized) Products.—Aging or oxidizing renders the products insoluble in rubber solvents, but they swell and soften, in some cases appreciably. The films do not appear to darken on aging. The oxidized products are similar in color to the soluble substances from which they were obtained and are still thermoplastic. These oxidized products are not tough and horny like the insoluble isomer, but are brittle, particularly when formed by the aging of the conversion product.

Prevention of Oxidation (Aging).—Tests carried out on the aging of films showed that Nonox NS. was the most efficient of a large number of substances tried. With 1% incorporated, the films when aged at 70° C. showed no tendency to brittleness until after 60 days. As 24 hours at 70° C. is usually regarded as equal to 6 months' ordinary aging in the case of rubber compositions, it is evident that there is no difficulty in protecting the conversion product in practice.

The second oxidation product is obtained by the action of hydrogen peroxide (100 vols.) in chloroform-acetic acid solution. This is a white amorphous thermoplastic substance. It was purified by precipitation from chloroform with acetone. Some rubber was treated by the same method[28] for comparison. Both products gave brittle transparent films. The essential difference between the oxidized rubber and cyclized rubber oxidized by (1) aging, etc., (2) hydrogen peroxide is shown in their relative solubilities:

Solvent	Hydrogen peroxide oxidation products		Cyclized rubber oxidized by aging
	Rubber	Cyclized Rubber	
Acetone	Very soluble	Insoluble	Slightly soluble
Alcohol	Very soluble	Insoluble	Insoluble
Acetic acid	Very soluble	Very soluble	Soluble
Chloroform	Very soluble	Very soluble	Soluble
Benzene	Sparingly soluble	Very soluble	Insoluble
Ether	Sparingly soluble	Slightly soluble	Slightly soluble

The iodine number of the rubber-hydrogen peroxide product was 80, whereas that of the corresponding cyclized material gave a figure of 95. These figures approximate to one-half the values for the conversion product, the figure for the rubber being actually lower. The proportion of double bonds has been still further reduced by oxidation and both the rubber and the conversion product tend towards figures of the same order.

An analysis of the conversion product oxidized with hydrogen peroxide gave the following figures as a result of two concordant determinations: C=81.72, H=10.86, and oxygen by difference 7.42. If these figures be compared with those for the product before oxidation, it will be seen that the carbon and hydrogen are now again in the C_5H_8 ratio and the oxygen considerably increased.

The increase in weight noted when a film is aged in an oven at 70° C. may

exceed 10% against approximately 8% in the case of the hydrogen peroxide product. $(C_5H_8)_2O$ will require approximately 10.3% oxygen, equivalent to an increase in weight of 11.8%. It has been shown[28] that rubber similarly oxidized with hydrogen peroxide contains 27% of oxygen, corresponding to its greater unsaturation.

Insoluble Isomer.—Materials which are considered to be the insoluble isomer have been produced unintentionally. Thus, reactions in the cold or at relatively low temperatures, those using insufficient reagent and those using rubber softened with cobalt linoleate all tended to produce an insoluble material. It is a white, horny, fibrous, unpowderable substance, decomposing without melting, and is virtually insoluble in all the usual rubber solvents as well as in alcohol and acetone. It is attacked by mineral oils but not by linseed oil and seems to be unaffected by strong alkali. Milled on hot rolls, it could be sheeted, but became relatively brittle when cold. With plasticizers such as tritolyl phosphate, petroleum jelly or chlorinated paraffin wax, it was not plasticized, but became friable.

Preparative Details of the Insoluble Isomer.—100 grams of crepe or smoked sheet is let down to a 20% solution in purified toluene in a Pfleiderer type mixer; 4% boron trifluoride in the form of the acetic acid complex is worked into it in the cold, and left overnight. Gelling is usually complete the next day. The mass may be dried out (when it will retain the reagent residue), or it may be well washed with water or dilute ammonia. In either case it is obtained as a white horny material, and if dried in thin layers can be obtained as a translucent film somewhat reminiscent of celluloid.

CONCLUSIONS

Boron trifluoride or materials which give rise thereto effect a "cyclization" of rubber in solution: that is, the product is less unsaturated than the original rubber.

A particular degree of conversion has been shown to give a tough material, which produces strongly adherent films possessing a high degree of alkali-resistance.

When used as a paint medium the material acts as an unsaponifiable "breather" and pigment protector, allowing (unlike "sealers") the passage of aqueous solutions. For this reason it appears suitable for use on plaster and concrete.

Analysis of the purified product indicates appreciable oxidation at some stage and it may be further oxidized by aging at raised temperature or by reagents such as hydrogen peroxide. The oxidation products are not identical.

The conversion product yields also a hard vulcanized product resembling hard vulcanized rubber, but less thermoplastic and containing less sulfur than hard rubber produced under the same conditions.

This work has been carried out on behalf of the Rubber Producers' Research Association, to whom the authors are indebted for permission to publish.

REFERENCES

[1] Staudinger, "Die Hochmolekularen Organischen Verbindungen—Kautschuk und Cellulose", Berlin, Springer, **1932**; Schulz, *Naturwissenschaften* **20**, 592 (1932).
[2] Thies and Clifford, *Ind. Eng. Chem.* **26**, 123 (1934).
[3] "Untersuchungen uber die Natürlichen und Künstlichen Kautschukarten", Berlin, Springer, **1932**; *Kolloid-Z.* **27**, 311 (1920); **30**, 176 (1922); *Gummi-Ztg.* **37**, 100 (1922); Kautschuk **2**, 1 (1926); **4**, 142 (1928); **5**, 9 (1929); Geer and Winkelmann, U. S. Patent 1,705,757 (1929).
[4] Fisher, *Ind. Eng. Chem.* **19**, 1325 (1927); U. S. Patent 1,605,180 (1926).
[5] Geer, U. S. Patent 1,617,588 (1927).
[6] Fisher and McColm, *Ind. Eng. Chem.* **19**, 1328 (1927).

[7] Robinson and Imperial Chemical Industries, Ltd., British Patent 339,398 (1930).
[8] Imperial Chemical Industries, Ltd., German Patent 585,446 (1933).
[9] Fisher and Winkelmann, U. S. Patent 1,782,140 (1930).
[10] *Ind. Eng. Chem.* **19**, 1033 (1927); Geer, British Patent 384,911 (1932); Bruson, U. S. Patent 1,846,247 (1932); Jones and Winkelmann, U. S. Patent 2,064,763 (1936); British Patent 467,772 (1937).
[11] Bruson, British Patent 285,071 (1928); 306,390 (1929); U. S. Patent 1,797,188 (1931).
[12] *Ind. Eng. Chem.* **26**, 123 (1934); Goodyear, British Patent 426,565 (1935); Wingfoot Corp. British Patent 455,495 (1936).
[13] Fisher, U. S. Patent 1,642,018 (1927).
[14] Hopff, Ebel, Wolf and I. G. Farbenind. A.-G., German Patent 549,759 (1932).
[15] I. G. Farbenind. A.-G., British Patent 347,108 (1931).
[16] Walz and I. G. Farbenind. A.-G., German Patent 535,687 (1931).
[17] Walpamur Co., Ltd., French Patent 752,502 (1934).
[18] Farmer, Rowe, Stevens and Rubber Growers' Assoc., British Patent 467,531 (1937).
[19] Reaney, British Patent 459,435 (1937).
[20] Bruson, U. S. Patent 1,846,247 (1932).
[21] Geer, British Patent 384,911 (1932).
[22] I. G. Farbenind. A.-G., British Patent 409,009 (1934).
[23] Bruson, U. S. Patent 1,853,334 (1932); 1,892,101 (1933).
[24] I. G. Farbenind. A.-G., British Patent 382,755 (1932).
[25] *Kautschuk* **4**, 185 (1928).
[26] Nieuwland, Vogt and Foohey, *J. Am. Chem. Soc.* **52**, 1018 (1930); Bowlus and Nieuwland, *J. Am. Chem. Soc.* **53**, 3835 (1931); Van der Meulen and Heller, *J. Am. Chem. Soc.* **54**, 4404 (1932); O'Leary and Wenzke, *J. Am. Chem. Soc.* **55**, 2117 (1933); Kroeger and Nieuwland, *J. Am. Chem. Soc.* **57**, 454 (1935 (1935); Meerwein, *Ber.* **66B**, 411 (1933).
[27] Stevens and Stevens, *J. Soc. Chem. Ind.* **48**, 55T (1929), obtained a figure of 64.2 for a sample of pale crepe.
[28] Mair and Todd, J. Chem. Soc. (London) **1932**, p. 386.

THE ULTRA-RAPID TESTING OF RUBBER

THE TESTING OF ITS OXIDIZABILITY IN ONE QUARTER OF AN HOUR *

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Steady improvements in industrial technique and the increasingly exacting requirements of manufacturing processes have brought about a need for the development of more and more rapid control tests, with the added stipulation that this rapidity must not involve any sacrifice of precision, reliability and reproducibility. It seemed to the present authors that the manometric method[1] might lend itself to this character of testing.

For the present, the object has been to confine the problem within strict limits, *i.e.*, to confine it to control testing during or after manufacture, basing the work on facts which have already been established[2], for example, that oxidizability is influenced by various incidents or errors which may occur during the preparation of a rubber mixture or during its vulcanization. The test will be limited to a manometric comparison[3] of a finely divided sample with a standard sample, the behavior of which has been previously established and which should be representative of all products made in conformity with this standard.

In a case of this kind, rapidity of testing is essential. Now, in previous tests which have already been described, the temperature was fixed at 80° C., and the mercury in the manometric tubes ascended at a relatively slow rate, so that it was in most cases necessary to wait several hours to obtain a definite indication of any changes taking place. But even if it has not appeared advisable up to the present time to exceed a temperature of 80° C. in laboratory research, there is no objection, when it is a case of simple comparison, to operating at a higher temperature. Experiments carried out on this basis[4] proved that by this means the rapidity of testing can be greatly increased; in fact it will be shown that by operating at 120° C. it is possible to obtain indications of the behavior of rubber in the space of about one quarter of an hour.

INFLUENCE OF TEMPERATURE ON THE RATE OF OXIDATION

The following representative mixture:

Smoked sheet	100
Stearic acid	1
Zinc oxide	5
China clay	40
Tetramethylthiuram disulfide	0.20
Benzothiazyl disulfide	0.25
Sulfur	2.5

was vulcanized for 10 minutes at 143° C., in the form of a slab 3 mm. thick, 12 cm. wide and 16 cm. long. The oxidizabilities at 70, 80, 90, 100 and 120° C. of samples cut from this slab were then measured. Table I gives the results of these tests. The readings indicated for each temperature are the average heights

* An original contribution to RUBBER CHEMISTRY AND TECHNOLOGY.

TABLE I

At 70° C.		At 80° C.		At 90° C.		At 100° C.		At 120° C.	
Hours of oxidizing heating	Ascent of mercury (mm.)	Hours of oxidizing heating	Ascent of mercury (mm.)	Hours of oxidizing heating	Ascent of mercury (mm.)	Hours of oxidizing heating	Ascent of mercury (mm.)	Minutes of oxidizing heating	Ascent of mercury (mm.)
24	83	2	20	1	26	½	40	10	49
48	149	4	39	2	52	1	74	20	123
72	208	9	75	4	96	2	134	30	195
96	272	33	239	6	138	4	266	40	273
120	340	50	387	9	200	5	336	50	340
Average hourly ascent...	3	Average hourly ascent...	8	Average hourly ascent...	22	Average hourly ascent...	67	Average hourly ascent..	408

to which the mercury ascended, as observed with several identical samples, the weight of which (1.49 gram) corresponded to 1 gram of actual rubber. It was shown in the previous work that, under such conditions, the magnitude of the errors in reading the manometric columns was about 10%, a precision which it is not necessary to exceed in the oxidation of such a heterogeneous substance as rubber.

It will be observed that the coefficient of acceleration is not constant; in fact a comparison at 10° intervals shows that it is 2.6 between 70 and 80° C., 2.7 between 80 and 90° C., 3.0 between 90 and 100° C., and 2.4 between 100 and 120° C. Although a systematic study of this coefficient of acceleration was not undertaken, the different experiments lead us to believe that, with a few exceptions, this coefficient is influenced by the temperature and the composition of the rubber mixture. However these variations are relatively slight, and it may be said that the rate of oxidation, as in the present case, is in general about 50 times greater at 120° C. than at 80° C.

COMPARISON OF A COMPOUND WITH ITS STANDARD

A. NORMAL COMPOUNDS

Following each time the same operations of weighing, mixing and vulcanizing, seven slabs of the preceding compound were prepared. The simultaneous testing of the oxidizability of samples cut from these seven slabs amounts to no more nor less than a comparison of six articles of a given type of manufacture with their standard. Table 2 shows that the reproducibility obtained under

TABLE II

Minutes of heating at 120° C. in oxygen		10′	20′	30′	40′	50′
Ascents of mercury in mm. for sample.	1	48	123	195	270	336
	2	47	122	195	272	342
	3	50	127	203	285	354
	4	51	119	188	262	325
	5	48	121	193	271	338
	6	48	119	190	263	329
	7	50	128	204	288	358
Maximum difference		8.1%	7.3%	8.1%	8.7%	9.7%

these conditions is well within the limits observed in testing different portions of the same slab. In Figure 1, the seven oxidation curves fall within the hatched area.

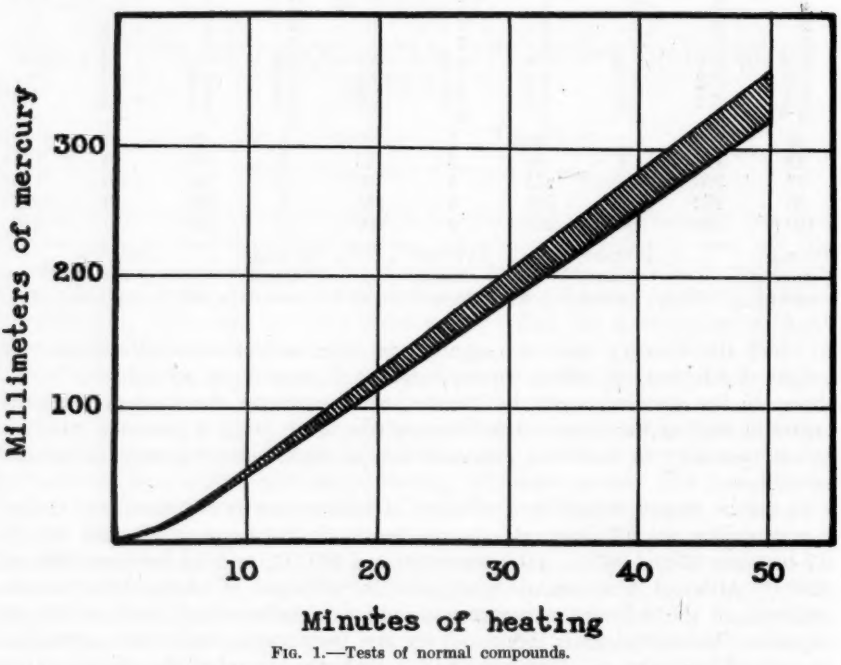

FIG. 1.—Tests of normal compounds.
The seven oxidation curves fall within the hatched area.

B. FAULTY COMPOUNDS

In contrast to this, a series of compounds were tested, in which various errors of manufacture were introduced intentionally.

Table III indicates their methods of preparation and the errors with respect to standard L_1.

TABLE III

Designation of mixture	L_1	L_2	L_3	L_4	L_5	L_6
Smoked sheet	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
China clay	40	40	40	40	40	40
Tetramethylthiuram disulfide	0.20	0.20	0.20	0.20	0.10	0.20
Benzothiazyl disulfide	0.25	0.25	0.25	0.25	0.25	0.25
Sulfur	2.5	2.5	2.5	5	2.5	2.5
Phenyl-β-naphthylamine	1	1	1	1	1	0
Time	8 min.	10 min.	8 min.	8 min.	8 min.	8 min.
Temperature	143° C.	143° C.	151°C.	143° C.	143° C.	143° C.
Mistake made	none (standard)	excessive vulcanization time	excessive vulcanizing temperature	double dose of sulfur	half dose of accelerators	omission of antioxygen

Oxidizability tests at 120° C. were made on 1.5-gram samples from these vulcanizates, a weight which corresponds to a net weight of 1 gram of actual rubber. Table IV and Figure 2 give the results obtained.

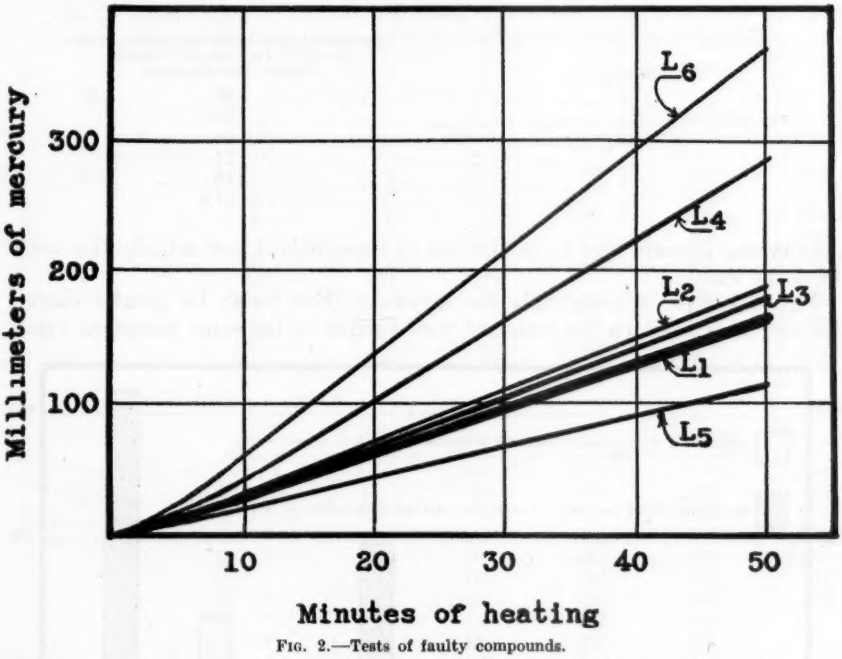

FIG. 2.—Tests of faulty compounds.

L_1 is the standard sample, whereas L_2, L_3, L_4, L_5 and L_6 are faulty in several respects.

It is evident that compounds L_6, L_4 and L_5 are faulty. In the case of L_2 and of L_3 the difference is very slight, and it exceeds only slightly the limits of variability of the test; consequently these limits should be regarded only as indicating a possible error.

The question then arises as to what ordinary specific gravity and hardness tests would have shown with these compounds? The specific gravity test, which could have given significant results only for L_4, L_5 or L_6, does not enable the detection of such slight errors.

TABLE IV

Minutes of heating at 120° C. in oxygen		10	20	30	40	50
Ascents of mercury in mm.....	L_1	26	62	97	131	167
	L_2	30	72	109	146	190
	L_3	29	68	106	143	185
	L_4	40	101	160	221	280
	L_5	18	42	66	90	115
	L_6	60	142	222	298	366

As for hardness tests, Table V gives the averages of four tests, made on the durometer of the Research Association of British Rubber Manufacturers, under normal operating conditions (penetration in 0.01 mm. of a ballbearing ¼ inch in diameter under a weight of 1 kg. applied for thirty seconds).

The errors in L_4 and L_5 are evident; but for L_2 and L_3 the variations from the standard are slight, and the indications given by the hardness test are not any better than those obtained by the oxidizability test. Lastly, L_6 (omission of

TABLE V

Sample	Hardness test with the durometer of the Research Association of British Rubber Manufacturers
L_1	86
L_2	89.5
L_3	90
L_4	74
L_5	119
L_6	87.5

antioxygen) appears here to be identical to the standard, but actually this is far from the case.

Figure 3 shows schematically the results of these tests; for greater clarity, the two tests made on the standard were carried to the same numerical value,

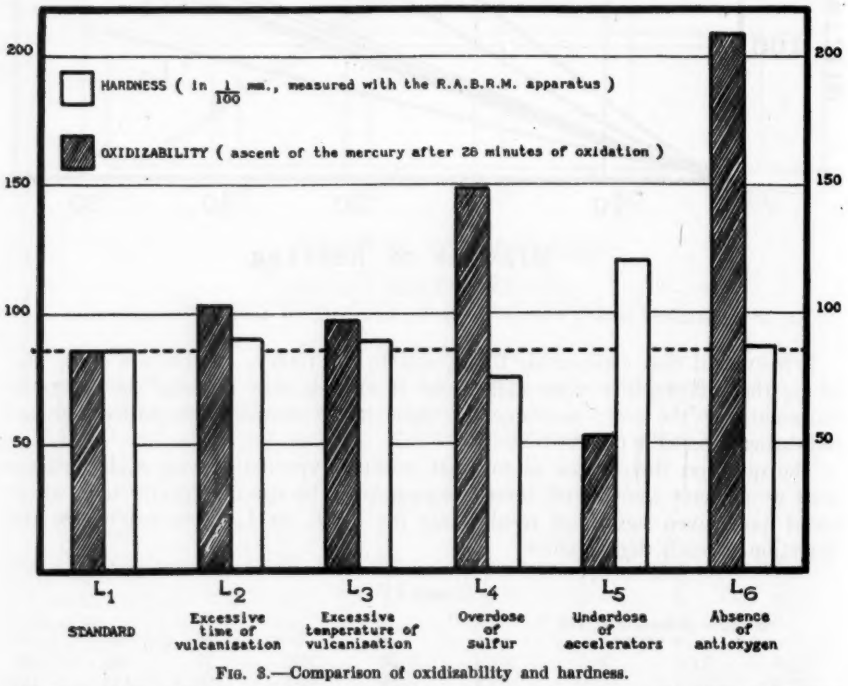

FIG. 3.—Comparison of oxidizability and hardness.

Hardness is in 0.01 mm. units, oxidizability as ascent of mercury in mm. after 28 minutes' oxidation. Deviations of L_2, L_3, L_4 and L_5 from the standard are evident in both the oxidizability and hardness tests; on the other hand, the hardness tests of L_6 do not indicate such deviations.

that is, the reading 86 was taken for the oxidizability of this standard, or an ascent after 28 minutes of oxidation.

INFLUENCE OF STATE OF SUBDIVISION

The great increase in the rate of oxidation gives rise to another problem, *viz.*, the influence of the state of subdivision. In reality, experience has shown that

the state of subdivision has but a slight influence in manometric tests at 80° C. and in all previous tests in glass apparatus at the same temperature. The rate of diffusion of oxygen through the rubber is therefore great compared to the rate of oxidation.

In the tests which are to be described this is not always so, and the higher the temperature the greater is the influence of the state of subdivision.

TABLE VI

Testing temperature	State of division	Ascent of mercury in mm. after oxidation of: 1 hr.	4 hrs.	8 hrs.	23 hrs.	31 hrs.
80° C.	1 piece	2	25	73	210	275
	2 pieces	3	30	73	208	278
	4 "	6	32	72	211	286
	16 "	7	30	71	199	266
	35 "	8	32	73	195	263
	64 "	11	35	74	196	263
	112 "	13	38	74	198	265
	210 "	16	41	80	199	266
	465 "	18	45	85	212	282
	Raspings	19	44	82	203	268

TABLE VII

Testing temperature	State of division	Ascent of mercury in mm. after oxidation of: 1 hr.	2 hrs.	4½ hrs.	5 hrs.	6 hrs.
100° C.	1 piece	13	58	172	202	254
	2 pieces	23	74	199	231	293
	4 "	44	106	235	266	325
	16 "	48	108	257	292	365
	30 "	49	111	257	295	371
	60 "	56	117	258	296	372
	103 "	67	135	297	340	—
	212 "	70	140	326	377	—
	481 "	77	149	366	400	—
	Raspings	79	154	367	400	—

TABLE VIII

Testing temperature	State of division	Ascent of mercury in mm. after oxidation of: 10 min.	20 min.	30 min.	40 min.	50 min.
120° C.	1 piece	0	11	27	46	65
	2 pieces	8	17	30	49	67
	4 "	37	74	114	155	196
	16 "	40	89	139	191	241
	29 "	50	99	150	201	252
	56 "	67	129	190	251	310
	107 "	96	166	241	315	382
	197 "	96	168	243	318	386
	478 "	119	222	328	—	—
	Raspings	120	227	336	—	—

The tests, the results of which are summarized in Table VI, were carried out at 80, 100 and 120° C. The compound used had the same properties as that in the tests on the influence of temperature. Strips were cut from slabs 3.2 mm. thick; they weighed 1.49 gram and were about 26 mm. by 11.5 mm. Each strip was then divided into a certain number of pieces. The sample designated as "raspings" was a coarse powder obtained by rasping rubber on a grindstone.

It will be seen from Tables VI, VII and VIII that at a temperature of 80° C. the differences observed at the beginning of oxidation gradually became equalized

and finally the state of subdivision had no influence on the results. On the other hand, the differences remained pronounced at 100° C., and were still more evident at 120° C.

Consequently in this type of oxidizability test, it is necessary to have as uniform samples as possible. The manner of cutting which has been used ordinarily gives about 100 pieces of sample; the deviations from this number have been small and have fallen within the limits of error. However, instead of this system of cutting, it would be preferable to use an instrument which would give small uniform cubes.

DESCRIPTION OF A REPRESENTATIVE TEST

To summarize the different results which have just been described, it may be said that an oxidizability test at 120° C. makes possible a rapid comparison of a given compound with its standard and, by only a few minutes' oxidation, makes it possible to decide whether or not they are identical.

In practical laboratory control, specific gravity and hardness tests give indications of errors in composition and vulcanization; the oxidizability test confirms these results and supplements them with an indication of the presence or absence of an antioxygen. Thus, Figure 2 shows that an omission of phenyl-β-naphthylamine in the L_6 compound is evident at the end of 5 minutes' oxidation by the ascent of mercury from 20 to 22 mm., in contrast to only 5 to 6 mm. when the proper dose of antioxygen is present.

However, it should be understood that the oxidizability test actually requires more time, since preliminary operations are necessary. To illustrate this, we shall describe an experiment that has been carried out for several months, as a classic test, for visitors at the *Palais de la Découverte,* in Paris. It demonstrates strikingly both the powerful effect of antioxygens and the rapidity of the test.

Rubber of good industrial quality, but without antioxygen, is previously divided into small uniform parallelopipeds about 2×2×3 mm.; a definite quantity is measured by a special container of known volume, and is put into a small glass receptacle A; a like quantity is poured into a test-tube containing finely powdered hydroquinone at the bottom; the tube is closed and shaken for a few moments; this rubber, with a little hydroquinone adhering to the surface, is then put into a second receptacle B.

Receptacles A and B are then placed in two cells of the manometer maintained at a temperature of 120° C., the stoppers are left half-open, and a current of oxygen, regulated by a flowmeter, is passed through the apparatus. These operations require a maximum of two minutes. This washing out by oxygen is continued for ten minutes, during which time the temperature becomes equalized throughout. At the end of this time, the tubes are sealed and the oxygen is shut off. Five minutes later, the mercury has risen to about 50 mm. for A and 10 mm. for B. The result is conclusive, and the experiment requires a total of 17 minutes.

It is no exaggeration to say it is possible to compare the oxidizability of different samples in about one quarter of an hour.

Theoretically there should be no disadvantage in increasing the rapidity of the test by changing the apparatus in certain ways, *e.g.,* the diameter of the manometric tube and the relative volumes of the reservoir and the sample. But this might lead to a sacrifice of precision for the sake of rapidity, without corresponding benefit; in reality, the test consumes much less than a quarter of an hour, and the operation is prolonged only on account of the ten-minute

"dead time" necessary for the required temperature to be reached. In a series of tests, this ten-minute dead period is not time lost, because with the manometer so constructed that its tubes function individually, this dead time can be utilized in preparing other samples.

CONCLUSION

It is hardly necessary to go into further detail to demonstrate the great advantages of such a test when used in a practical way.

In the control laboratory, it will supplement and confirm the various other routine tests and, most important, immediately detect an error which the other tests will not do, particularly the omission, insufficiency or incomplete distribution of antioxygen. It will also reveal the presence of harmful impurities.

For specifications and in manufacture, it will enable the article itself to be tested, either by removing a small piece or by providing a cavity for this purpose in the mould.

Of course it is not necessary to limit the testing time to a quarter of an hour. If greater differences in the manometric levels are desired, the oxidation curve may be continued for a longer period, one hour, for example.

Finally this oxidizability test at 120° C. would appear to fulfill the requirements of rapidity and precision of control testing, at least in the present state of stability of rubber products. Only in case of greatly increased resistance to oxidation would it be necessary to prolong the test for more than one quarter of an hour.

REFERENCES

[1] Ch. Dufraisse, *Proc. Rubber Tech. Conference*, London, **1938**, p. 547.
[2] Ch. Dufraisse and J. Le Bras, *Proc, Rubber Tech. Conference*, London, **1938**, p. 555.
[3] Ch. Dufraisse, *Rubber Chem. and Tech.* **11**, 268 (1938).
[4] Ch. Dufraisse and J. Le Bras, *Proc. Rubber Tech. Conference*, London, **1938**, p. 571.

THE T-50 TEST FOR STATE OF VULCANIZATION. II *

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INTRODUCTION

In industry the control of state of vulcanization of a rubber product is very important with reference to the quality of the merchandise. For example, an undervulcanized tire is not only objectionable in appearance, due to the sulfur bloom, but is also likely to give poor service with respect to resistance to wear, separation and other failures. On the other hand, an overvulcanized tire is more susceptible to deterioration from oxidation and is, therefore, less desirable than one properly vulcanized. The same limitations, with respect to degree of vulcanization, apply to elastic thread, rubber footwear, clothing and many other articles.

Among the older criteria of degree of vulcanization, free or combined sulfur and the tensile strength or modulus of the rubber have been employed. The physical tests, such as modulus or tensile strength, are still in universal use, and in many cases they are well adapted to the control of the state of vulcanization. Disadvantages of physical tests are the difficulty of obtaining a sample of satisfactory size, the inability to predict whether or not the article will bloom, and the fact that other variables such as filler or softener content affect the physical properties. Therefore, it is frequently necessary to make free sulfur determinations in order to be sure that the free sulfur content is safely below the concentration which will result in bloom.

The T-50 test for state of vulcanization[1] has the advantage that it is a very rapid test which can be made on a small sample of vulcanized rubber. In addition, it not only gives an index to the state of vulcanization in a manner similar to combined sulfur, but also can be used to gauge the free sulfur content. In compounds which contain sulfur-bearing fillers such as barytes and lithopone, which would interfere with the chemical analysis for combined sulfur, the T-50 test is of exceptional value since it is not affected by inert fillers. The test is not an absolute measure of the state of vulcanization, since for each type of compound tested it requires calibration against vulcanizates of known combined-sulfur content, if it is to be used as a quantitative measure of combined sulfur. The T-50 test is not unique in this respect, since other tests, physical and chemical, are not universal tools for the measurement of state of vulcanization. Indeed, the definition of state of vulcanization or state of cure is not general, but is limited to a specific compound. Whitby[2] states, "the term 'state of cure' is intended to indicate the position of a cure in a series of progressive cures." The T-50 test, however, even without calibration, does afford an accurate measure of the relative states of vulcanization in a series prepared from any one rubber compound.

Application of the T-50 test is restricted to those types of compounds which can be stretched 300% or more. Thus, heavily compounded rubber articles such as soles and tiling cannot be tested. Lack of sensitivity for some compounds containing more than 4% of combined sulfur restricts the use of the T-50 test.

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 36, pages 861-867.

The T-50 value decreases steadily with increased vulcanization of soft rubber compounds, *i.e.*, the T-50 value decreases as the combined sulfur increases. The T-50 values correlate better with the percentage of combined sulfur based on the rubber content of the stock (*i.e.*, smoked sheet or pale crepe, not rubber hydrocarbon) than with percentage of combined sulfur based on the weight of the sample of a rubber compound. Therefore, it is desirable to express sulfur contents on the former rather than on the latter or customary basis. This convention broadens the basis for the usefulness and simplifies the interpretation, especially in similar compounds which vary in filler content.

It is the object of this paper to present T-50 data and analytical data for sulfur content on a series of widely different "pure-gum" soft rubber compounds in order to study the relation of the T-50 values of these compounds at different degrees of vulcanization with the total combined sulfur and with the corrected combined sulfur, which is the total combined sulfur corrected for that part which has combined with zinc oxide in the compound.

THE T-50 TEST

Briefly, the procedure for the T-50 test consists of stretching a piece of rubber, preferably to within 100% of its ultimate elongation, chilling it to a low temperature while stretched, and releasing it. The rubber remains elongated. As the temperature of the rubber is gradually raised it retracts. The temperature (°C.) at which it has lost 50% of its original elongation is observed. This temperature is referred to as the T-50 value. The T-50 value for raw rubber is approximately 18° C. The greater the degree of vulcanization the lower is the temperature. In many compounds most of the retraction occurs in a fairly small temperature range; consequently in routine work the determination of the T-50 value is quite rapid when the approximate state of vulcanization is known. The details of the procedure in carrying out the test have been previously described[1].

MODIFICATIONS OF THE T-50 TEST

Various modifications of the T-50 test have been developed since the original publication. For example, an apparatus using a horizontal pan and sample rack in place of the Dewar flask and vertical sample rack has been described[3]. This type of equipment is in use in a number of laboratories. It gives the same results as the original form of apparatus.

An alternative method, which has not been previously described, consists in dipping the stretched samples into a bath of fixed temperature in the neighborhood of the T-50 temperature. This method is of advantage only in large-scale control testing on a production basis. When this method is used, the lengths of the test-pieces in the fixed temperature bath are empirically calibrated against the T-50 value determined according to the original technique.

USES OF THE T-50 TEST

In addition to the use of the T-50 test in controlling the degree of vulcanization of merchandise, it has been used[3] for the evaluation of anti-scorch materials, as a control test for effect of the variability in strength of accelerators, and to show variation in effect of fillers such as carbon black and whiting on the rate of vulcanization of rubber, variation in state of vulcanization of extremely low sulfur compounds which are difficult to analyze, variability in the activating strength of reclaims and variability in the rate of vulcanization of plantation

rubber and also latex films. In a very complete description and illustration of the application of the T-50 test to compounds containing zinc oxide[4], the conclusion is reached that the T-50 value is an extremely satisfactory tool for the study of the

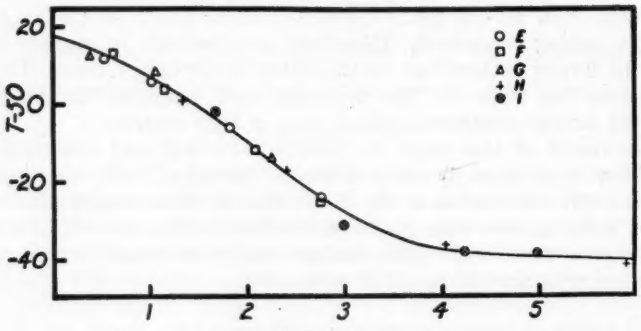

FIG. 1.—Grams total combined sulfur per 100 grams rubber.

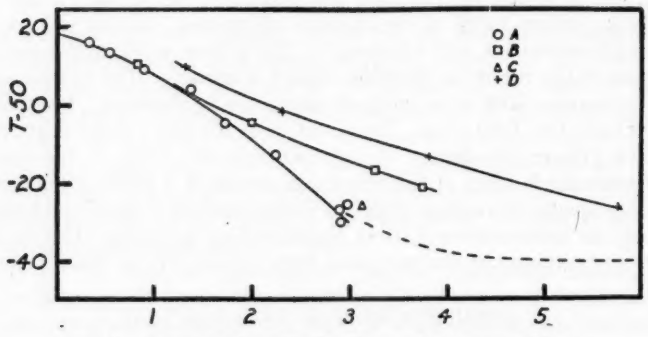

FIG. 2.—Grams total combined sulfur per 100 grams rubber.

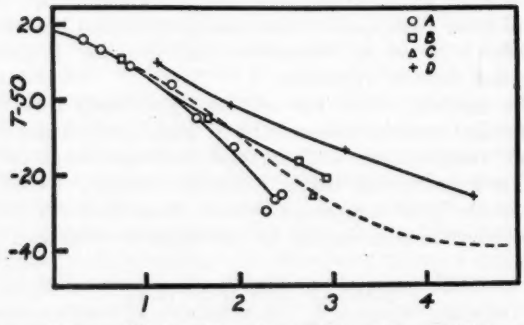

FIG. 3.—Grams total combined sulfur minus sulfide sulfur per 100 grams rubber.

effect of zinc oxides on the rate of vulcanization. For example, there are marked differences in vulcanization rate between various zinc oxides in stocks containing more than 10 parts of pigment in 100 parts of rubber. Zinc oxides containing sulfur show marked retardation, as do the fine oxides, at high loadings. In addition, the T-50 test can be used as a sensitive indicator of uniformity of

temperature in a multiple-platen hydraulic press used in the vulcanization of rubber. The T-50 test can be applied also to the study of the rate of vulcanization or variability of vulcanization of goods vulcanized in the vapor of sulfur chloride or in cold vulcanization compounds. On account of the speed of the test and precision of the results the T-50 test is very useful, and in many cases is more desirable than combined sulfur or free sulfur determinations or measurements of the physical properties.

THE T-50 TEST WITH DIFFERENT TYPES OF COMPOUNDS

It has been stated[1] that the T-50 value decreases as the extent of vulcanization increases, *i.e.*, with time of vulcanization or with extent of combined sulfur. In many cases there is good correlation between the T-50 test and combined sulfur computed on the basis of the rubber content of the compound. The rule that a drop of 13° C. for the T-50 value represents an increase of approximately 1% of combined sulfur was stated to be subject to variations; for example, in compounds containing reclaim, in the case of reverted vulcanization, and in some cases where ultra-accelerators are employed. In this paper it is desired to present data for vulcanizates containing four different accelerators and for a typical unaccelerated compound.

EXPERIMENTAL

The compounds chosen were of widely different types in order to illustrate the largest possible variations. For example, compounds with 3 and 6 parts of sulfur, respectively, per 100 parts of rubber, with and without zinc oxide and also with different typical accelerators were employed.

The recipes are shown in Table I.

TABLE I

Recipe	A	B	C	D	E	F	G	H	I
Rubber (smoked sheet)	100	100	100	100	100	100	100	100	100
Sulfur	3	3	6	6	3	3	6	6	6
BLE	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Stearic acid	3.75	3.75	3.75	3.75	—	—	—	—	—
Zinc oxide	3	3	6	6	—	—	—	—	—
BJF	0.75	—	—	—	0.75	—	—	—	—
Beutene	—	0.5	—	—	—	0.5	—	—	—
Pentex	—	—	0.6	—	—	—	0.6	—	—
Polyamine accelerator	—	—	—	1	—	—	—	1	—

BLE—Ketone-diarylamine condensate (antioxidant).
BJF—Phenylaminomethylbenzothiazyl sulfide (accelerator).
Beutene—Butyraldehyde-aniline condensate (accelerator).
Pentex—Thiuram derivative (accelerator).

In Table II are given the T-50 values, total combined sulfur, total combined sulfur minus sulfide sulfur, 500% modulus, tensile strength and elongation at break. The T-50 values were determined according to the standard procedure[1] except for the elongation. The elongation values are tabulated. The total combined sulfur was determined on the acetone-extracted vulcanizates by modification of Wolesensky's method[5]. Sulfide sulfur was determined according to a modification of Stevens' method[6]. The 500% modulus was taken from a stress-strain curve drawn with a special stress-strain machine of the Schopper type, employing a circular test piece. The tensile strengths and elongations at break were obtained with a Scott stress-strain machine. Dumb-bell test-pieces were used.

In Fig. 1, with T-50 value as ordinate and total combined sulfur (g. per 100 g. of rubber) as abscissa, a curve is drawn through points for compounds E, F, G, H and I, which contain 3 or 6 parts of sulfur per 100 parts of rubber with different accelerators and no zinc oxide. In this case no correction of the total combined sulfur for sulfide sulfur is necessary.

TABLE II

Recipe	Minutes vulcanized	T-50	% Elongation in T-50 test	Total combined sulfur (g./100 g. rubber)	Total combined sulfur minus sulfide sulfur (g./100 g. rubber)	500% modulus (lbs./sq. in.)	Tensile strength (lbs./sq. in.)	Elongation at break %
A	5 at 142° C.	+ 13.5	800	0.56	0.53	—	—	—
	10 " "	+ 4.1	800	1.39	1.28	350	3140	840
	20 " "	− 12.6	800	2.24	1.94	665	4390	790
	45 " "	− 25.2	800	2.97	2.45	780	4066	760
	90 " "	− 29.8	800	2.91	2.28	610	3793	750
	10 " 121° C.	+ 16.1	800	0.35	0.35	—	—	—
	30 " "	+ 9.2	800	0.91	0.84	—	—	—
	60 " "	− 4.8	800	1.73	1.54	—	—	—
	240 " "	− 26.6	600	2.89	2.37	—	—	—
B	10 at 142° C.	+ 10.6	800	0.85	0.75	375	2930	830
	20 " "	− 4.8	800	2.00	1.66	700	4555	800
	45 " "	− 16.4	650	3.25	2.63	1050	4450	740
	90 " "	− 21.0	800	3.75	2.92	690	3785	780
C	10 at 142° C.	− 25.5	500	3.12	2.78	1900	4265	690
D	10 at 142° C.	+ 9.8	800	1.33	1.13	475	2839	800
	20 " "	− 1.6	800	2.31	1.91	690	3468	770
	45 " "	− 13.4	500	3.81	3.13	1040	3908	710
	90 " "	− 26.2	500	5.75	4.51	1620	3615	630
E	10 at 142° C.	+ 11.8	800	0.55	—	60	626	1050
	20 " "	+ 5.8	800	1.03	—	80	828	1150
	45 " "	− 6.0	800	1.82	—	115	1049	1100
	90 " "	− 24.2	800	2.76	—	100	1541	1000
F	10 at 142° C.	+ 13.0	800	0.64	—	—	1151	1070
	20 " "	+ 3.8	800	1.16	—	150	1768	1060
	45 " "	− 11.8	800	2.08	—	200	2245	1000
	90 " "	− 25.5	800	2.75	—	—	2224	990
G	20 at 142° C.	+ 12.9	800	0.40	—	50	209	1170
	45 " "	+ 8.5	800	1.07	—	125	1051	1070
	90 " "	− 13.8	800	2.25	—	—	1900	1000
H	10 at 142° C.	+ 0.8	800	1.34	—	250	1982	830
	20 " "	− 17.2	800	2.40	—	300	2297	840
	45 " "	− 35.8	800	4.03	—	500	3131	800
	90 " "	− 41.6	500	5.90	—	—	3125	800
I	60 at 145° C.	− 2.0	800	1.68	—	140	1427	1050
	120 " "	− 31.3	800	2.99	—	200	2407	1030
	180 " "	− 38.0	800	4.23	—	250	3054	960
	240 " "	− 38.5	800	4.98	—	—	3117	940

In Fig. 2, with T-50 value as ordinate and total combined sulfur (g. per 100 g. of rubber) as abscissa, curves (in addition to the dotted curve of Fig. 1) are shown for compounds A, B, C and D containing zinc oxide and 3 or 6 parts of sulfur and different accelerators.

In Fig. 3, with T-50 as ordinate and total combined sulfur minus sulfide sulfur (g. per 100 g. of rubber) as abscissa, curves are shown for the zinc oxide accelerated compounds A, B, C and D in comparison with the dotted curve of Fig. 1.

DISCUSSION

In Fig. 1, which shows the relationship between the T-50 values and the total combined sulfur for the various compounds which contain no zinc oxide, it is seen that there is a very good correlation in different compounds between the T-50 values and the combined sulfur determinations, which is independent of the composition. On the other hand, in Fig. 2, different compounds which contain zinc oxide do not, in general, give the same relationship between the T-50 and the total combined sulfur. The T-50 values of a specific compound, however, do correlate well with the combined sulfurs. This illustrates the empirical nature of the T-50 test.

In compounds containing zinc oxide it is common knowledge that zinc sulfide is formed during vulcanization. Without doubt this sulfide sulfur is not combined with the rubber. It was thought that it would be interesting to investigate whether or not the T-50 values of different compounds would give a better correlation with the corrected combined sulfur, namely, grams total combined sulfur minus sulfide sulfur per 100 grams rubber, than with the total combined sulfur. It is evident from the data shown in Fig. 3 that the correlation of the T-50 value of different compounds with the corrected combined sulfur is no better than with the total combined sulfur.

In Table II are given physical properties of the vulcanizates in addition to the T-50 values and sulfur data. It is evident that the T-50 values correlate better with the combined sulfur data than with the physical properties. Nevertheless, the T-50 values can be correlated with the physical properties of a specific compound and used to control them.

The advantage of the T-50 test is primarily in the speed of testing. It can readily be used to estimate rapidly the state of vulcanization of a rubber compound which has been calibrated in terms of chemical analysis or physical properties.

SUMMARY

The uses and applications of the T-50 test for state of vulcanization have been listed.

New combined sulfur data corrected for sulfur combined as zinc sulfide have been presented.

The T-50 values for vulcanizates which contain no zinc oxide, but which are widely different in composition, give identical curves when plotted against the total combined sulfur.

The T-50 values for vulcanizates which contain zinc oxide and which are widely different in composition do not give identical curves when plotted against either the total or the corrected combined sulfur.

REFERENCES

[1] Gibbons, Gerke and Tingey, *Ind. Eng. Chem., Anal. Ed.* **5**, 279 (1933).
[2] Whitby, "Plantation Rubber and the Testing of Rubber," Longmans, London **1920**, pp. 320 and 340.
[3] Tuley, *India Rubber World* **97**, 39 (1937).
[4] Haslam and Klaman, *Ind. Eng. Chem., Anal. Ed.* **9**, 552 (1937).
[5] *Ind. Eng. Chem.* **20**, 1234 (1928).
[6] *Analyst* **40**, 275 (1915).

A MACHINE FOR THE SYSTEMATIC TESTING OF RUBBER SUBJECTED TO REPEATED FLEXINGS *

LUCIEN GRAFFE

The machine which is described in this communication was designed, after due consideration from both the theoretical and practical points of view, to flex rubber samples repeatedly without subjecting them to longitudinal traction, *i.e.*, to flex them at constant length.

The test-piece, cut in the form of strips from a sheet or from some particular part of an article, is fastened at each end; one end is held immovable, the other is fastened to a movable support which undergoes reciprocal motion.

There seems to be no record of the existence of a machine of this type, in fact most specifications call for tests involving repeated traction. At a recent international rubber conference F. Jacobs described a machine with which test-specimens of special shape can be alternately flexed and subjected to impact, which has an influence on the results. Moreover this machine requires moulded test-specimens, so that it is impossible to test samples prepared from articles in the particular forms in which they are designed for service.

At first thought it might be assumed that this machine operates in such a way that the samples are not subjected to longitudinal traction during flexing. In reality, since every deformation of a solid body involves a change in the arrangement of the elementary fibers, and since rubber is apparently no exception to this rule, a sequence of tensions and compressions occurs, the frequency of which is the same as that of the reciprocating motion; the amplitude can be changed at will, and the intensity of the stresses depends on the particular conditions, as the brief analysis which follows will attempt to show.

In this analysis an endeavor is made to take into account the nature of the phenomena and their order of magnitude by studying first of all the deformation of a rubber band bent over upon itself in the way to be described.

A strip of rubber (density 1.25), cut from a sheet 3 mm. thick, was attached to the surface of a cylinder covered with paper (marked in millimeters) in such a way that it adhered as well as possible without pressure to part of the circumference.

Before attaching the rubber strip in this way, it was laid flat and on it were drawn parallel lines 10 mm. apart; the cylinder was faced with paper, with a circumferential length of 80 mm., corresponding to a diameter of 25.47 mm.

Thus the semi-circumference was 40 mm., and then by taking 40 mm. as a basis of reference on the rubber, it was easily possible to estimate, on the one hand, the difference between the line of contact of the curved rubber and the charted paper, and on the other hand the change on the outside surface of the stretched rubber by means of an ordinary commercial thin steel ribbon marked in millimeters.

By this means it could readily be shown that the interior concave surface contracted and the outside surface elongated. This is shown diagrammatically in Figure 1.

* Translated for Rubber Chemistry and Technology from the Revue Générale du Caoutchouc, Vol. 15, No. 10, pages 358-362, December, 1938. This mémoire received the 1938 prize of the Rubber Society (Syndicat du Caoutchouc).

If the total thickness E remained unchanged, the semi-circumferences CE and CI would be, respectively:

$$\tfrac{1}{2}\ CE = \frac{\pi(D+2E)}{2} = \frac{\pi D}{2} + \pi E$$

$$\tfrac{1}{2}\ CI = \frac{\pi D}{2}$$

The difference: $CE - CI = \pi E$ is independent of D. In the present case E was 3, so that πE was 9.42.

Actually measurements gave:

$$\tfrac{1}{2}\ CE = 46$$
$$\tfrac{1}{2}\ CI = 36.7$$
$$\text{Difference} = 9.3$$

Consequently the stretched fibers exerted on the whole rubber strip a pressure in the direction toward the center of curvature. This pressure was however not uniformly distributed, as can be seen by the form of the transverse section

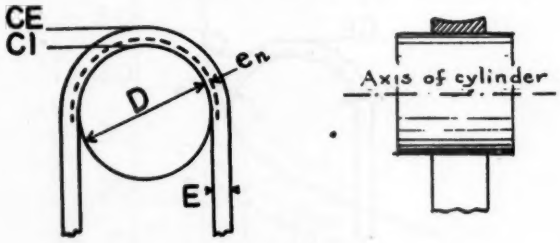

FIG. 1.

(represented in Figure 1), which is no longer the same as that of the original cross-section. This cross-section becomes somewhat concave on the outside and also becomes narrower, while it widens and bulges slightly on the inside surface of the curvature. It is evident then that with rubber these deformations are decidedly complex.

CIRCUMFERENTIAL TENSIONS AND COMPRESSIONS

If these deformations, the magnitudes of which are less than the degree of approximation of the measurement described, are considered abstractly, it is found that the maximum tension T exerted on the outside surface of a strip of rubber of original length L_o 40 mm. and thickness e 3 mm. in the circumferential direction is:

$$T = CE - L_o$$
$$= 46 - 40$$
$$= 6 \text{ mm.}$$

i.e., 15 per cent.

The compressive force M in the circumferential direction on the inside surface is:

$$M = L_o - CI$$
$$= 40 - 36.7$$
$$= 3.3$$

i.e., 8.25 per cent.

If it is assumed that the neutral axis is at a distance e_n, then:

$$\frac{e_n}{e} = \frac{3.3}{6+3.3}$$

where $e_n = 1.06$.

In another measurement e_n was found still closer to unity.

In a further experiment with a thinner band ($e = 2.5$), with the same radius of curvature, the following results were obtained:

Elongation of outside elongated periphery	12 per cent
Contraction of inside compressed periphery	6.25 per cent
Position of the neutral axis e_n	0.83

It is evident then that flexing of a strip of rubber sets up two unequal zones, the tension zone being thicker than the compression zone. When the radius of curvature is at least four times as great as the thickness of the test-strip, the compression zone is about one-third of the total thickness of the rubber strip.

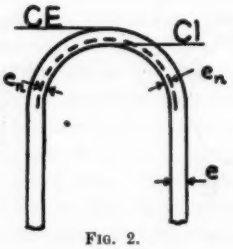

FIG. 2.

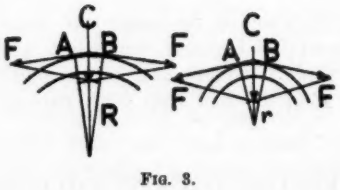

FIG. 3.

INFLUENCE OF THE RADIUS OF CURVATURE

The same samples, or rather samples of the same quality, were then attached around cylinders of smaller diameters. The following results were obtained with samples 3 mm. thick.

Diameter of cylinder (mm.)	14	10	6
Circumferential elongation (percentage)	25	30	50
Contraction (percentage)	15	20	25
e_n	1.12	1.20	1.22

Hence when the radius of curvature is made smaller, and flexure is intensified as a result, the surface elongation and contraction increase, while the neutral line extends so that the zone of compression becomes greater. This is shown diagrammatically in Figure 3.

In view of the fact that any increase in elongation of rubber is accompanied by an increase in tension, it is possible to explain this shift in the neutral line by considering an arc between two points, A and B, very close together on the surface, and extended the same distance AB apart but on two arcs of different radii R and r. These two points A and B are subjected to two forces F and F which are equal and opposite, meet at point C, and are tangent to the outer curve. Their resultant G is greater on curve r than on curve R, as is evident in Figure 3.

Irrespective of their actual values, it was proved in these experiments that the elongation, and consequently also the tension, to which the rubber is subjected are not very large. An examination of the curves shown in Figure 4, which summarizes the results, will show that the elongation on the surface increases almost asymptotically as the radius of curvature decreases, while the latter approaches a limit which is the thickness of the rubber itself. This as-

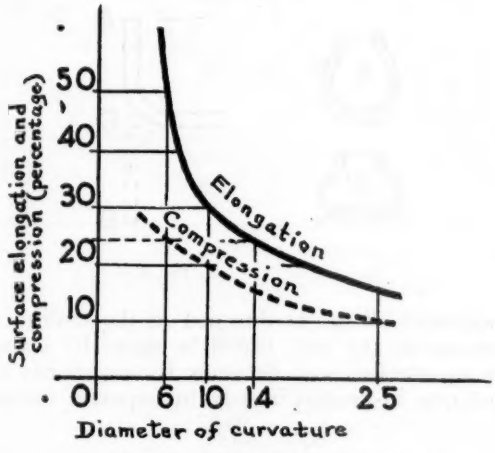

FIG. 4.

sumes of course that the total flexure is realized, but actually this is not so in practice, for the interior bent surface cannot be reduced to zero.

In one of the most common of all cases of repeated flexing, *i.e.*, the sidewalls of pneumatic tires, the maximum radii of curvature of the active zone close to the ground are never less than 20 mm. However, the natural curvature of the cross-section must be taken into account, and the work expended in flexing corresponds only to the differences between the radii of curvature R and R′ of the section in its normal state and when flattened (see Figure 5). Now under service conditions soft rubber elongates only 15 to 20 per cent, and this is far below its ultimate elongation, which may be above 600 per cent.

The formation of cracks and fissures must then be attributed to other causes, such as fatigue from hysteresis, heterogeneous composition, changes in the surface, etc., all of which can be traced more or less directly to irregularities of manufacture.

A machine so designed that it will reveal these phenomena and at the same time operate under conditions as close as possible to service conditions of the particular rubber product, and finally with only a limited number of variables,

would then be unquestionably of interest. With its aid it should be possible to explain certain doubtful points in connection with premature changes which take place in rubber subjected to mechanical forces.

DISCUSSION

In developing machines for flexing or stretching rubber repeatedly, designers have endeavored to combine the various causes of fatigue, either by subjecting test-specimens to constant elongation or by subjecting them alternately to flexure and to compression (AO and OB in Figure 6), as in testing metals, whereby the stretched surfaces are alternately compressed and stressed.

Although the machine designed by the present author can operate under these conditions, this does not seem to represent the conditions which rubber ordinarily undergoes in service. As a matter of fact, neither in the flexing of pneumatic tires nor the sole and shank of footwear do the repeated flexings change

FIG. 5.

FIG. 6.

direction, and a repeated change in direction of the flexing only complicates and obscures unnecessarily any test. It will be shown by a few typical results that it is possible to establish very definitely the superiority or inferiority of one product in relation to another merely by repeated flexings in the same direction.

DESCRIPTION OF THE MACHINE

The description which follows refers to the diagrams (see Figure 7) and to the photographs (see Figures 9 and 10). Figure 7 represents an elevation and a plan.

The test-specimen is attached at one end to a horizontal plate H and is secured by a bolted plate B. The other end A of the test-specimen is fastened to a horizontal rod, which is attached to a beam F which oscillates through the arc AA′.

The movement of this beam is actuated by means of an eccentric E mounted on a shaft driven by pully G; this eccentric is connected to the beam by means of a square axis A_o and a crank the length of which can be varied by adjusting screw V. This crank is provided with an elongated slot, and the more this is shortened, the more is the amplitude of motion of the beam increased.

An electric motor M, the speed of which is controlled by a rheostat R, drives pulley G by means of a reducing pulley P with two grooves.

A revolution counter, C, records the number of revolutions of the shaft and eccentric and thereby the number of oscillations of the beam. Because of the great number of oscillations, counter C is geared down and its readings are multiplied by a constant factor.

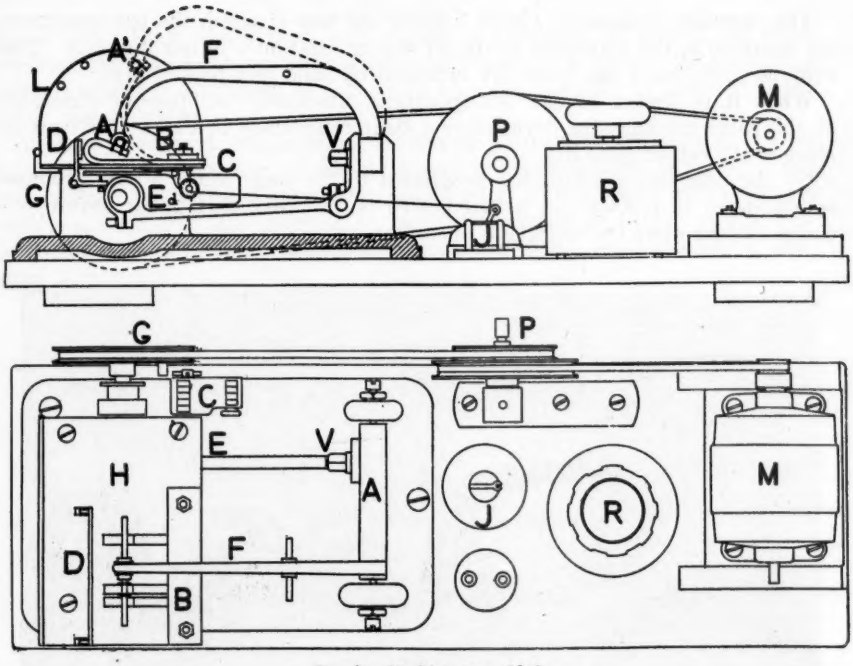

FIG. 7.—Machine assembled.

FIG. 8.

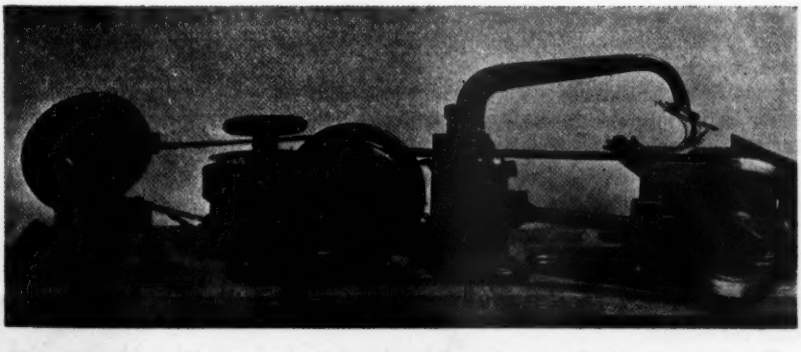

FIG. 9.—Machine operating at room temperature.

The assembly depicted in Figure 7 shows the way in which the test-specimens are mounted in the apparatus ready for flexing constantly in one direction. The extreme positions of the beam are indicated by solid and broken lines.

When it is desired to flex test-specimens alternately in opposite directions on this same machine, the device shown diagrammatically in Figure 8 is used in place of the bolted plate B.

By the time that cracking has progressed to the stage where a test-specimen is considered to have failed, a lengthening of the bent part under flexure becomes evident while the machine is operating.

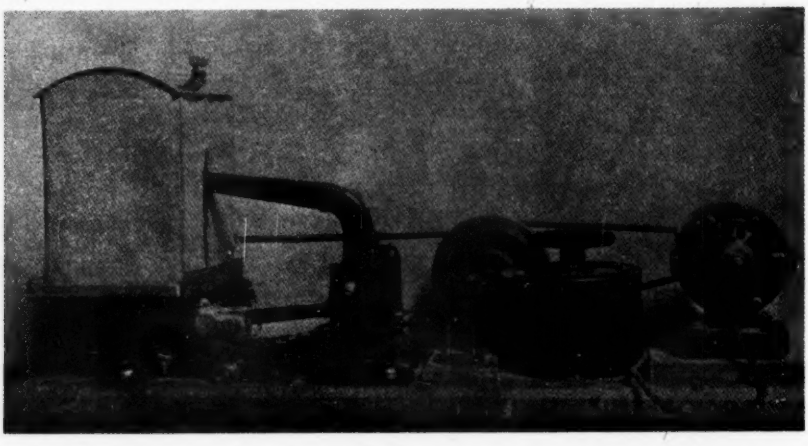

FIG. 10.—Machine operating with hot air.

SPEED

The universal type of motor operates equally on direct and alternating current, and with the particular assembly described, it is possible to operate at speeds of the order of 10,000 to 80,000 revolutions per hour, or an equivalent number of oscillations.

A calculation of the number of times that any point of an automobile pneumatic tire (2 meters in circumference in contact with the ground) close to the ground is flexed gives a value of the order of 30,000 flexures per hour for a speed of 60 kilometers per hour, and 50,000 flexings per hour for a speed of 100 kilometers per hour.

It is evident therefore that the new machine does work on test-specimens under conditions similar to those under which the rubber in the sidewalls of pneumatic tires is flexed in service.

Finally a hood L, mounted on table H, and equipped with electric heating resistances on the inside, forms a hot-air oven, in which the test-specimens can be maintained at any desired elevated temperature during flexing (see Figure 10).

The tabulated data which follow are some results with test-specimens of different compositions, before and after accelerated aging, and show the concordant results which can be obtained in repeated tests on the same samples under the same conditions.

The mixtures which were tested in this way had a total rubber content of

56 per cent. They were chosen with a view to obtaining an idea of the effect of adding vulcanized rubber scrap to these mixtures. As is known, the reclaiming of scrap rubber is a problem of economics which is rightfully of concern to the rubber manufacturer.

The base mixture A contained, as mentioned, 56 per cent of rubber, the remaining 44 per cent being accessory ingredients and mineral fillers. To this base mixture were added increasing proportions of vulcanized rubber scrap, which was itself originally mixture A. Mixture B contained 10 per cent of vulcanized mixture A as scrap, mixture C contained 16 per cent, mixture D contained 20 per cent.

	Sample			
	A	B	C	D
Before aging				
Tensile strength (kg.)	1.250	1.200	1.150	0.835
Elongation at rupture (%)	875	835	780	640
After aging				
Tensile strength (kg.)	1.140	1.100	0.880	0.440
Elongation at rupture (%)	850	750	710	570

REPEATED FLEXURE

(Number of flexings)

		Incipient cracking	Rupture
A	Before aging	1,060,000	1,228,000
	After aging	455,000	723,000
B	Before aging	700,000	1,099,000
	After aging	570,000	773,000
C	Before aging	680,000	887,000
	After aging	203,000	384,000
D	Before aging	67,000; 80,000; 90,000	89,000; 89,000; 113,000
	After aging	19,400	32,000
E	Mixture A with 30% of coarsely ground scrap	14,600	26,300
F	Mixture E refined	30,600	45,000
G	Mixture E with finely ground scrap	450,000	608,000

The samples were first tested for tensile strength and elongation at rupture before and after an accelerated aging test of 10 days in air at 70° C. The same samples were then tested, likewise before and after artificial aging, on the new flexing machine described in the present paper.

The tabulated results show that the incorporation of vulcanized rubber scrap into products designed to withstand flexing should be done very cautiously and only when the scrap has been prepared especially for the purpose.

Finally from a more general point of view, it can be shown that resistance to flexing, even if it is of the same relative order as tensile strength, is far from being comparable to it. Continued flexing involves factors of its own, such as hysteresis, heterogeneity, heat effects, etc.

THE KOH-NUMBER TEST AND ITS APPLICATION TO THE COMPOUNDING OF ZINC OXIDE IN RUBBER LATEX *

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INTRODUCTION

It is well known that zinc oxide thickens and destabilizes ammonia-preserved latex. In order to reduce the magnitude of this effect in compounding latex with zinc oxide, various types of stabilizers have been used, including proteins, sulfonated organic compounds and alkalies. It is known also that the stability of zinc oxide compounds is increased by reducing the ammonia concentration with formaldehyde.

This paper is concerned with the stabilization of zinc oxide compounds by reduction of ammonia content and by control of the *p*H with fixed alkali. It has been found that the amount of fixed alkali required to obtain optimum physical and storage properties in zinc oxide compounds may be determined by electrometric titration of the latex. This KOH requirement varies greatly, depending on the lot, type and purity of the uncompounded latex. Part I is concerned with the theoretical requirements for stabilization of zinc oxide compounds, and Part II with the experimental application of electrometric titration methods to the fulfilment of these requirements.

PART I. THEORETICAL

A. FACTORS AFFECTING THE STABILITY OF LATEX.

Latex may be considered to consist of particles of rubber hydrocarbon surrounded by an outer protective layer of one or more proteins[1], and suspended in a solution containing soaps, amino acids and salts, part of which may be adsorbed. Its stability, as in the case of similar colloids, is dependent on the degree of hydration of the protein shell and the electrostatic charge on the latex particle. Hydration cannot at present be subjected to direct measurement in latex, but this is not essential for present purposes, since most of the experimental results can be explained in terms of factors affecting particle charge.

As a first approximation, the cataphoretic mobility of a colloid may be used as a measure of the particle charge. Hence, the cataphoretic mobility can be considered as a direct index of the colloidal stability when the hydration is constant. In order to determine the effects of *p*H, salt concentration and other factors on the electric charge of latex particles, extensive measurements of cataphoretic mobility have been made by the single particle method in these laboratories by C. P. Roe. In general, the experimental technique was the same as that described by Abramson[2], and the rubber content of the suspensions investigated was approximately 0.02%. A paper on this subject will be published at a later date.

Figure 1 shows the variation of cataphoretic mobility with *p*H in uni-univalent

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 51, pages 111-125.

buffers and di-univalent buffers, respectively, at constant ionic strength. Curves I-A, B and C are for latex particles suspended in potassium buffer solutions of monobasic acids at ionic strengths of 0.05, 0.1 and 0.2, respectively. Curves II-A and B are for latex particles suspended in calcium buffer solutions of monobasic acids at ionic strengths of 0.05 and 0.1, respectively. The following points are of interest.

1. In solutions of constant ionic strength the mobility increases with pH between the isoelectric point and pH=8, but is insensitive to further increases in pH.

2. Latex particles in dilute solutions of potassium or calcium salts of monobasic acids are negatively charged above pH 4.2, but the mobility (and hence the charge) is far less in the calcium buffer solutions than in the potassium buffers at the same pH and ionic strength. This indicates a strong adsorption of the divalent calcium ions by the particles and explains the known destabilizing action of calcium compounds on latex. Other divalent cations, such as Zn^{++} and Ba^{++}, would be expected to produce similar effects.

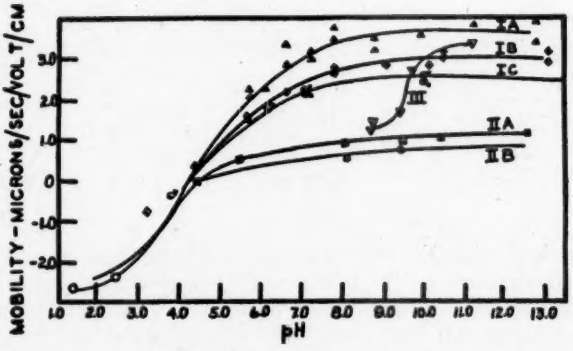

FIG. 1.

3. At constant pH the mobility of latex particles in potassium buffers varies inversely as the square root of the ionic strength.

4. If it is assumed that the mobility of latex particles in di-univalent buffers also varies inversely as the square root of the ionic strength, it may be calculated that for latex particles to have the same mobility in a calcium buffer as in a potassium buffer of ionic strength=0.1, the ionic strength of the calcium buffer must be approximately 0.006. This, of course, corresponds to a concentration of calcium ion equal to 0.002 M.

The correspondence between mobility and latex stability is obvious from a consideration of the preceding facts. It is well known that latex coagulates in the region of the isoelectric point, and is unstable below pH 8. The destabilizing action of divalent ions, such as Ca^{++}, has been untilized in certain latex processes. Experimental evidence, to be published later, shows that the stability of latex decreases with increasing ionic strength much in the same way as does the mobility. Hence, the conclusion may be drawn that in order to obtain stability in a latex compound containing zinc oxide, the concentration of divalent zinc ion must be of the order of 0.002 M or less.

In order to illustrate further the conditions to be met in compounding zinc oxide, mobility measurements were made on latex particles in solutions containing 0.83% NH_3 and 0.11% zinc ion, in which the pH was varied by addition

of HCl. These results are illustrated in Curve III of Figure 1. Below *p*H 9 the mobility is small[3]—comparable with that in the calcium buffers—and approaches a maximum value between *p*H 10.5 and 11. This behavior can be explained on the assumption that "zinc-ammonia hydroxide," like zinc hydroxide, has two widely different basic dissociation constants which are approximately equal to those of zinc hydroxide. This would mean that divalent zinc-ammonia ion is gradually converted into monovalent zinc-ammonia hydroxide ion as the *p*H is increased between 8 and 11, with the half transformation point at *p*H 9.6 (see Eq. 2 below). The conditions favoring a minimum concentration of divalent zinc or zinc-ammonia ion may be more exactly defined by further consideration of the mass action equations involved.

B. Conclusions Based on Mass Action Equations.

Zinc oxide in aqueous systems is in equilibrium with zinc hydroxide, which dissociates in steps as follows:

$$ZnO(s) \rightleftarrows Zn(OH)_2 \rightleftarrows ZnOH^+ + OH^- \rightleftarrows Zn^{++} + 2OH^-$$

For the preceding equilibria the following equations[4] may be written:

$$(ZnOH^+)(OH^-) = K_1 \tag{1}$$

$$\frac{(Zn^{++})(OH^-)}{(ZnOH^+)} = K_2 (= 4.4 \times 10^{-5}) \tag{2}$$

$$(Zn^{++}) = \frac{K_1 K_2}{(OH^-)^2} = \frac{4 \times 10^{-18}}{(OH^-)^2} \tag{3}$$

Equation 3 shows that the concentration of divalent zinc ion decreases 100-fold for each unit increase in *p*H. It can easily be calculated from Equation 3 that in water solution the concentration of divalent Zn^{++} ion is only 4×10^{-4} at *p*H 7, and that at higher *p*H levels the concentration should be far below the safe maximum of 2×10^{-3} indicated by the mobility measurements. However, in latex the solubility of zinc oxide is increased by the ammonia, ammonium salts, and (possibly) amino acids, and attention must therefore be given to the mass-action equations of the zinc-ammonia hydroxides.

Zinc oxide dissolves in ammonia and for present purposes may be considered to dissociate as follows:

$$Zn(OH)_2 + 4NH_3 \rightleftarrows Zn(NH_3)_3OH^+ + OH^- + NH_3 \rightleftarrows Zn(NH_3)_4^{++} + 2OH^-$$

The concentration of divalent zinc-ammonia ion is given by the equation:

$$(Zn(NH_3)_4^{++}) = K_4 \frac{(NH_3)^4}{(OH^-)^2} \tag{4}$$

Also

$$\frac{(Zn(NH_3)_3OH^+)}{(Zn(NH_3)_4^{++})} = K_5 \frac{(OH^-)}{(NH_3)} \tag{5}$$

Equation 4 shows that the concentration of divalent zinc-ammonia ion increases as the fourth power of the concentration of ammonia, and decreases inversely as the square of the hydroxide ion concentration. Equation 5 shows that the ratio of monovalent zinc-ammonia hydroxide ion to divalent ion is directly proportional to the hydroxide ion concentration and inversely proportional to the ammonia concentration. This emphasizes the importance of maintaining the ammonia concentration at the lowest level, and the *p*H at the highest level, con-

sistent with other compounding considerations. However, as will be shown in a later section, it is undesirable to reduce the ammonia or to increase the *p*H beyond certain limits.

PART II. EXPERIMENTAL

A. Titration of Latex with Fixed Alkalies—The KOH Number.

McGavack and Rumbold[5] showed that latex contains the ammonium salts of amino acids, and that a titration curve with a well defined end-point is obtained by electrometric titration of latex with fixed alkali, using the glass electrode. The writer and his coworkers have found that the KOH titer of latex is affected by many factors, including the source and degree of purification of the latex, and that it defines the optimum quantity of KOH for stabilization of zinc oxide compounds.

Typical electrometric titration curves, obtained by titration of a normal latex with 0.5 *N* KOH using the glass electrode, are given in Figure 2. Curve A is for a sample of the latex titrated at its original ammonia content of 1.25%. Curves B and C are for samples of the same latex in which the ammonia was reduced to 0.2% and 0.0%, respectively, by the addition of formaldehyde[6], and Curve D for a sample containing a slight excess of formaldehyde. These curves are similar in shape to those for an acid of *p*H equal to about 9.5 titrated in the presence of corresponding amounts of ammonia, and have well defined points of inflection at a *p*H value of approximately 11. *The quantity of KOH corresponding to this point of inflection, in grams of KOH added per* 100 *grams of latex solids, is defined as the KOH number.* Thus the KOH number is a measure of the titratable acidic components in latex referred to the solids content.

Figure 2 shows that as the ammonia present during titration is decreased, the latex buffers at lower *p*H levels, the rate of change of *p*H with added KOH becomes greater, and the inflection in the curve becomes more pronounced. If excess formaldehyde is added, the latex buffers at a still lower *p*H (presumably due to conversion of the amino groups of amino acids, polypeptides, etc., into less basic methyleneimino groups), and the inflection becomes somewhat less pronounced. It has, therefore, become a standard practice in these laboratories to reduce the ammonia in the latex to approximately 0.2% before titration. The end point can often be selected with somewhat greater accuracy from the maximum in the differential curve:

$$\left(\frac{\Delta\, p\mathrm{H}}{\Delta\, \mathrm{KOH}} \text{ plotted against added KOH}\right).$$

Unless proper precautions are taken, the ammonia adjustment with formaldehyde liberates CO_2 from ammonium carbonate in the latex and induces a lower observed KOH number. This can be avoided by adding to the latex before ammonia adjustment an amount of KOH sufficient to maintain the *p*H above 9, which, incidentally, prevents local flocculation. The amount of KOH required for this is about 15% of the KOH number. The values of the KOH numbers from the curves in Figure 2, which are listed below, show that under proper experimental conditions the KOH number is independent of the ammonia concentration during titration, within the limits of experimental error.

	NH_3	KOH No.
Curve A	1.25%	1.94
B	0.2%	1.88
C	0.0%	1.88
D	xs CH_2O	1.90

The KOH number is, of course, independent of the concentration of the latex during titration. In order to permit easy cleaning of the glass electrode, concentrated latices are diluted with distilled water to 30-35% total solids before titration.

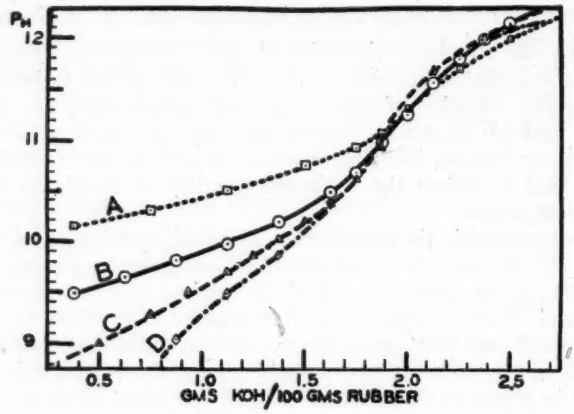

FIG. 2.

As would be expected, the KOH number is reduced by creaming or centrifuging from a lower to a higher solids content. This is illustrated by the following KOH number data for a sample of latex which was creamed repeatedly from 33% total solids to approximately 60% total solids.

Times creamed	% T.S. of concentrate	KOH No. (obs.)	KOH No. (calc.)	% Original serum per 100 rubber remaining in concentrate
0 (Normal)	44.7	1.77	(1.77)	100
1	60.5	0.60	0.62	32.2
2	59.8	0.24	0.26	10.68
3	58.2	0.15	0.14	3.77

Thus more than a tenfold decrease in KOH number can be produced by creaming three times between the limits stated. If it is assumed that chemicals adsorbed on the latex are equivalent to 0.08 KOH number units, and only the remainder are subject to removal, the KOH number of a purified latex may be calculated from that of the original as follows: KOH No. (B) = 0.08 + ([KOH No. (A) − 0.08] × fraction original serum remaining).

The KOH number of a given type of latex (*i.e.*, normal or concentrated) is by no means constant. Commercially available normal latices vary in KOH number between 1.2 and 2.4 and creamed and centrifuged concentrates between 0.55 and 0.95. This variation in KOH number has been found to be responsible for much of the difficulty encountered in the past in duplicating latex compounds from one lot to another.

It should be emphasized that the apparent KOH number of latex preserved with fixed alkali is not an index of quality. In such cases the true index of quality is given by the apparent KOH number plus the initial fixed alkali content referred to the rubber.

Another point of importance is that latex containing an ammonium soap for stabilization will have a KOH number which is higher by an amount equivalent to the soap added.

B. Application of the KOH Number Principle to Zinc Oxide Compounds.

1. *Simple Compounds containing only Zinc Oxide and Sulfur.*

The KOH number has been found to be extremely important in compounding, since it defines the amount of KOH required to give the optimum physical and storage properties to latex compounds containing zinc oxide. In order to illustrate this fact a series of zinc oxide compounds containing a constant low amount of ammonia (0.15% of the rubber content) and varying amounts of KOH was made from each of three latices with KOH numbers of 0.51, 0.96 and 0.14, respectively. KOH number titration curves for these latices are given in Figure 3.

Table I

	FAA	FAB	FAC	FAD	FAE	FAH *	FAF	FAG
Latex solids (A) (KOH No. = 0.51)	100							
KOH	0.15	0.30	0.45	0.60	0.75	0.85	1.0	1.5
Final NH_3	0.15							
Sulfur	2.0							
Zinc oxide	3.0							
T.S.	58%							
Tested after 16 *hours.*								
*p*H	9.50	9.88	10.61	11.58	12.03	12.16	12.36	12.60
Viscosity η (centipoises)	25.7	28.4	26.0	30.3	32.4	32.8	35.5	32.5
Yield value F_0 (cg./cm.^{2})	2.0	0.8	0.1	0.0	0.1	1.1	0.0	0.0
Mechanical stability (min.)	1.6	3.9	>10	>10	1.3	1.1	1.0	0.7
Tested after 21 *days.*								
*p*H	9.39	9.56	10.30	11.12	11.68	11.84	11.92	12.24
Viscosity η (centipoises)	33.0	31.0	27.0	28.0	30.0	35.4	33.0	27.0
Yield value F_0 (cg./cm.^{2})	1.6	1.1	0.3	0	0	0	0	0.2
Mechanical stability (min.)	1.3	3.8	>10	4.2	0.9	0.7	0.7	0.7

* The compound FAH was made from the same latex as the other compounds in this series. It was, however, prepared three weeks later than the others. Tests on the aged compound FAH were carried out after 16 days instead of after 21 days.

The first two were centrifuged concentrates having the lowest and highest KOH number values ordinarily encountered in compounding practice. The third was a three times creamed latex. In order to keep the system as simple as possible, sulfur and zinc oxide were the only rubber compounding ingredients added. The formulas and physical test data for the compounds are given in Tables I, II, and III.

The procedure used in compounding was as follows: To the latex was first added the KOH as a 20% solution. The ammonia content was then reduced to 0.15%, referred to the rubber, by the addition of formaldehyde diluted with sufficient water to give a final total solids content of 58% in the compound. The sulfur and zinc oxide were then added as ball-milled pastes containing 3% of casein and 3% of Darvan No. 1, respectively, based on the solids content. The protective ingredients in the pastes were kept at a minimum in order to render their effect on the *p*H of the latex compound insignificant. The compounds were mixed with a propeller type stirrer and were de-aerated for 16 hours under a vacuum of approximately 27 inches of mercury before being tested.

The *p*H, viscosity, yield point and mechanical stability were measured according to the methods previously described by Jordan, Brass, and Roe[7], after the

compounds had stood 16 hours and 3 weeks, respectively. The results are illustrated graphically in Figures 4, 5 and 6, in which the solid lines and broken lines are for compounds aged 16 hours and 3 weeks, respectively.

TABLE II

	FCA	FCB	FCC	FCD	FCE	FCF	FCK *	FCG	FCH	FCI	FCJ
Latex solids (B) (KOH No. = 0.96).	100										
KOH	0.2	0.4	0.6	0.8	1.0	1.2	1.3	1.6	0.2	0.9	1.2
Final NH_3	0.15	—	—	—	—	—	—	—	1.0	1.0	1.0
Sulfur	2.0										
Zinc oxide	3.0										
T.S.	58%										
Tested after 16 hours.											
*p*H	9.21	9.62	10.02	10.53	11.44	12.03	12.26	12.45	10.52	11.53	12.22
Viscosity η (cp.)	62.1	37.4	33.7	31.2	36.1	38.1	41.4	35.9	38.9	34.3	38.9
Yield value F_0 (cg./cm.^{2})	3.0	2.0	0.1	0.9	0.0	0.2	0.0	0.4	0.0	0.0	0.0
Mechanical stability (min.)	0.3	0.7	1.4	3.4	4.7	1.0	0.9	0.7	0.6	3.3	0.8
Tested after 21 days.											
*p*H	9.08	9.54	9.95	10.42	11.15	11.62	11.90	12.12	10.47	11.38	11.99
Viscosity η (cp.)	Too thick	83.0	64.0	39.0	38.0	39.0	42.6	38.0	80.0	35.0	42.0
Yield value F_0 (cg./cm.^{2})		2.6	1.6	0.5	0.0	0.9	0.5	0.3	2.3	0.0	0.5
Mechanical stability (min.)	0.3	0.6	1.3	2.6	3.5	0.7	0.7	0.6	0.4	2.3	0.6

* The compound FCK was made from the same latex as the other compounds in this series. It was, however, prepared three weeks later than the others. Tests on the aged compound FCK were carried out after 16 days instead of after 21 days.

TABLE III

	FEA	FEB	FEC	FED	FEE	FEF	FEI *	FEG	FEH
Latex solids (C) (KOH No. = 0.14)	100								
KOH	0	0.05	0.10	0.15	0.20	0.40	0.50	0.60	1.00
Final NH_3	0.15								
Sulfur	2.0								
Zinc oxide	3.0								
T.S.	58%								
Tested after 16 hours.									
*p*H	9.91	10.24	10.55	11.18	11.48	12.26	12.28	12.35	12.40
Viscosity η (cp.)	27.0	27.6	27.7	29.4	32.4	38.0	36.8	36.2	37.0
Yield value F_0 (cg./cm.^{2})	1.5	1.2	1.5	1.2	0.8	0.6	1.8	0.8	0.8
Mechanical stability (min.)	2.1	7.6	>10	>10	>10	1.2	0.8	0.7	0.5
Tested after 21 days.									
*p*H	9.82	10.16	10.46	11.06	11.18	11.87	12.15	12.26	12.35
Viscosity η (cp.)	27.1	28.9	28.3	28.7	30.5	33.1	35.1	35.2	38.8
Yield value F_0 (cg./cm.^{2})	1.8	0.7	0.9	1.3	1.3	1.5	1.1	1.8	2.0
Mechanical stability (min.)	1.7	7.1	>10	>10	>10	1.1	0.7	0.6	0.4

* The compound FEI was made from the same latex as the other compounds in this series. It was, however, prepared three weeks later than the others. Tests on the aged compound FEI were carried out after 16 days instead of after 21 days.

The curves for the variation in *p*H of freshly prepared compounds with added alkali are similar in shape to the titration curves for the uncompounded latices and have inflection points corresponding to the KOH numbers. This is to be expected, of course, since none of the compounding ingredients added buffer

appreciably between *p*H 9.0 and *p*H 11.5. On standing, the *p*H values decrease slightly in the *p*H region between 9.8 and 11.5, and to a somewhat greater extent at higher *p*H levels.

The mechanical stability, as would be expected from the discussion in the previous sections, is very low in compounds having a *p*H value less than 9.8, and increases to a maximum value at a *p*H of approximately 11.0, corresponding to an amount of added alkali equivalent to the KOH number. The maximum mechanical stability value is lower for the latex having the highest KOH number than for those with the lower KOH numbers. Some of the compounds with *p*H values in the region 10.5-11.0 have mechanical stability values above 10 minutes (these are designated by arrows attached to the symbols around the plotted

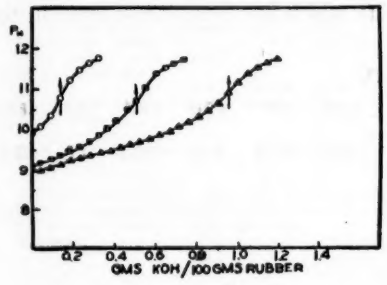

FIG. 3.

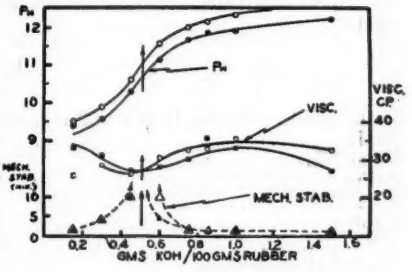

FIG. 4.

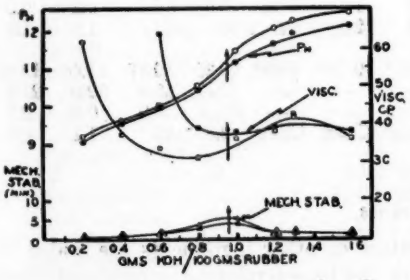

FIG. 5.

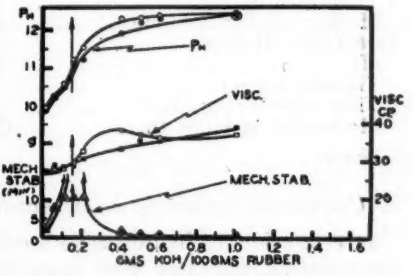

FIG. 6.

points). The test was not continued to ultimate coagulation in these cases, since it has been found by experience that compounds with mechanical stability values greater than 10 minutes are suitable for most practical purposes where stability is desired. As the KOH content is increased above *p*H 11.0, the stability falls sharply and is very low in every case above *p*H 12. The stability values decrease slightly on aging.

The viscosity of the freshly prepared compounds has a minimum value between approximately *p*H 9.8 and 11.0, but in general is higher on either side of this region. The minimum viscosity value is approximately the same for the latices having the two lower KOH numbers, and is slightly higher for the one having a KOH number of 0.96. The increase in viscosity at higher *p*H levels can hardly be attributed to a simple salt effect, since it is not a function of the KOH number and therefore of the total salt concentration. The viscosity values of compounds with *p*H values less than 9.8 increase on standing, and the in-

crease at a given *p*H level becomes greater as the KOH number of the latex is higher. The change in viscosity on standing is insignificant from a practical standpoint in compounds with *p*H values above 10.7.

By way of summary, in simple zinc oxide compounds the *p*H required for minimum viscosity, maximum stability and minimum change during storage is obtained by adding an amount of KOH equivalent to the KOH number of the latex. Thus the KOH number, in addition to being an index of quality of the latex, defines quantitatively the amount of KOH required for optimum stabilization of zinc oxide compounds in the absence of added buffering ingredients. It is obvious that if any one given amount of KOH were used for stabilization of compounds from all three latices, regardless of their KOH number, wide variations in properties would result. It is believed that lack of proper appreciation of the latter fact explains much of the difficulty which has been encountered in the past.

TABLE IV

	FBA	FBB	FBC	FBD	FBE	FBF	FBG
Latex solids (A) (KOH No. = 0.51)	100						
KOH	0.15	0.30	0.45	0.60	0.75	1.0	1.5
Final NH_3	0.15						
Sulfur	2.0						
Zinc oxide	3.0						
Captax	1.0						
T.S.	58%						
Tested after 16 *hours.*							
*p*H	9.47	9.81	10.14	10.37	10.75	11.99	12.57
Viscosity η (cp.)	35.0	30.7	26.6	24.7	27.3	33.3	30.8
Yield value F_0 (cg./cm.^{2})	2.3	1.6	0.4	0.9	0.4	0.2	0.0
Mechanical stability (min.)	1.4	2.5	4.8	>10	>10	1.9	1.0
Tested after 21 *days.*							
*p*H	9.37*	9.78*	9.89*	10.20	10.57	11.46	12.01
Viscosity η (cp.)	—	—	—	Too	32.0	32.0	27.0
Yield value F_0 (cg./cm.^{2})	—	—	—	thick	0.9	0.0	0.0
Mechanical stability (min.)	Coag.	Coag.	Coag.	2.8	>10	1.1	0.8

* Serum.

2. *Compounds containing Acidic Accelerators.*

In case acidic or hydrolyzable accelerators or other ingredients are added in compounding, allowance must be made for the base-combining capacity of these materials. In order to illustrate this point 1.0 part of Captax per 100 parts of rubber was added, as a ball-milled paste containing 0.15 part of Darvan No. 1 per part of Captax, to each of the simple compounds described in the previous section. The formulas and test data for the compounds thus obtained are given in Tables IV, V and VI, and the latter are illustrated graphically in Figures 7, 8 and 9.

The figures show that in shape the *p*H curves are similar to those for the simple compounds previously discussed, with the exception that the point of inflection is shifted to a value which is higher by approximately 0.3 KOH number units. This, of course, corresponds to the amount of KOH which is stoichiometrically equivalent to the Captax. The *p*H values of aged compounds decrease slightly in the region below *p*H 11.0 and to a somewhat greater extent above this point. The viscosity goes through a minimum corresponding to a *p*H of 10.4-10.5. The increase in viscosity on aging becomes progressively greater as the *p*H is reduced below 10.5, but is reasonably constant above this point. Furthermore, the change in viscosity which occurs on the aging of compounds at a given *p*H value increases with increase in KOH number of the latex.

The mechanical stability increases as the *p*H is increased above *p*H 9.5, and reaches a maximum value corresponding to a *p*H of approximately 10.6-10.7. The maximum stability, as in the previous case, is lower for the latex having

TABLE V

	FDA	FDB	FDC	FDD	FDE	FDF	FDK*	FDG	FDH	FDI	FDJ
Latex solids (B) (KOH No.=0.96).	100										
KOH	0.2	0.4	0.6	0.8	1.0	1.2	1.3	1.6	0.2	0.9	1.2
Final NH_3	0.15	—	—	—	—	—	—	—	1.0	1.0	1.0
Sulfur	2.0										
Zinc oxide	3.0										
Captax	1.0										
T.S.	58%										
Tested after 16 hours.											
*p*H	9.12	9.52	9.83	10.18	10.41	10.86	11.06	12.22	Coag.	11.05	11.49
Viscosity η (cp.)	Too	100.7	39.5	34.4	40.3	33.6	33.7	35.5	—	46.5	34.1
Yield value F_0 (cg./cm.^{2})	thick	5.5	1.5	1.4	1.4	0.9	1.1	0.0	—	3.1	0.1
Mechanical stability (min.)	0.2	0.6	1.2	1.8	2.9	6.7	6.3	1.1	—	1.5	4.9
Tested after 21 days.											
*p*H	8.91†	9.39†	9.79†	10.10	10.34	10.61	10.99	11.73	Coag.	10.87	11.29
Viscosity η (cp.)	Coag.	Coag.	Coag.	Too	Too	50.7	43.4	33.6	—	65.5	36.8
Yield value F_0 (cg./cm.^{2})	—	—	—	thick	thick	1.4	1.3	0.0	—	2.6	0.0
Mechanical stability (min.)	—	—	—	0.6	1.4	5.9	5.7	0.6	—	1.0	1.9

* The compound FDK was made from the same latex as the other compounds in this series. It was, however, prepared three weeks later than the others. Tests on the aged compound FDK were carried out after 16 days instead of after 21 days.
† Serum.

TABLE VI

	FFA	FFB	FFC	FFD	FFE	FFF	FFI*	FFG	FFH
Latex solids (C) (KOH No. = 0.14)	100								
KOH	0.0	0.05	0.10	0.15	0.20	0.40	0.50	0.60	1.00
Final NH_3	0.15								
Sulfur	2.0								
Zinc oxide	3.0								
Captax	1.0								
T.S.	58%								
Tested after 16 hours.									
*p*H	9.69	9.92	10.07	10.23	10.34	10.71	11.48	11.90	12.43
Viscosity η (cp.)	34.2	31.4	29.8	29.4	27.3	29.0	29.4	34.2	33.4
Yield value F_0 (cg./cm.^{2})	2.7	1.7	2.2	1.3	1.0	0.5	1.3	1.2	1.0
Mechanical stability (min.)	1.3	2.4	4.8	8.0	9.6	>10	>10	1.0	0.4
Tested after 21 days.									
*p*H	9.67	9.81	9.86	10.08	10.14	10.52	11.15	11.34	12.20
Viscosity η (cp.)	49.1	35.3	35.1	31.1	28.9	27.0	30.1	31.7	35.8
Yield value F_0 (cg./cm.^{2})	2.4	3.1	2.2	2.2	1.8	2.2	0	0.5	1.5
Mechanical stability (min.)	1.1	2.2	4.6	7.6	8.7	>10	>10	1.0	0.3

* The compound FFI was made from the same latex as the other compounds in this series. It was, however, prepared three weeks later than the others. Tests on the aged compound FFI were carried out after 16 days instead of after 21 days.

the highest KOH number than for the other two. The stability of compounds with *p*H values less than 10.3 decreased considerably on aging, and compounds with *p*H values less than 9.6-9.7 coagulated.

By way of summary, it is seen that, in the case of Captax compounds, the optimum viscosity and storage properties are obtained in compounds at *p*H values between 10.5 and 10.7. *p*H values in this interval are obtained when the

amount of added KOH is equal to the KOH number plus approximately two-thirds the amount required to neutralize the Captax. Further experimental information on the alkali requirements for various types of accelerators will be published at a later date.

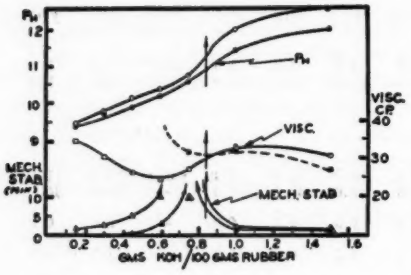

FIG. 7.

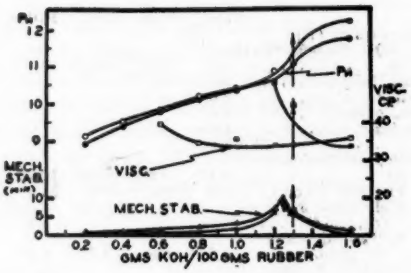

FIG. 8.

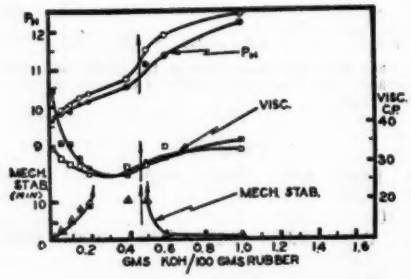

FIG. 9.

Many of the common compounding ingredients, such as glue, casein and gum arabic, are capable of combining with bases, and if appreciable amounts of these are used in compounding, the KOH content of the compound must be increased accordingly. In the following table data obtained from titration curves are given for the amount of KOH required per gram of protective ingredient at different *p*H levels.

	Approximate g. of KOH per g. of protective to raise *p*H to value given		
*p*H	A-1 casein	Gum arabic	Glue
9.0	0.05	0.005	0.02
9.5	0.05	0.01	0.03
10.0	0.05	0.012	0.04
10.5	0.07	0.02	0.04
11.0	0.08	0.07	0.05
11.5	0.09	0.20	0.06

3. *Effect of Ammonia Content.*

The effect of ammonia content on the properties of simple zinc oxide compounds is illustrated by compounds FCH, FCI and FCJ, which contain 0.2, 0.9 and 1.2 parts of KOH, respectively, and an ammonia content of 1.0 part per 100 parts of latex rubber. The formulas and test data given in Table II, and are to be compared with those for compounds FCA and FCG.

The titration curves previously discussed for latices at various ammonia contents (Fig. 2) showed that in the region below *pH* 11 the *p*H corresponding to a given amount of KOH increased as the ammonia was increased. The same is, of course, true for latex compounds. Thus compound FCH, with high ammonia, has a much higher *p*H (10.5) and a correspondingly lower viscosity than the corresponding low ammonia compound FCA (*p*H=9.21). A comparison of compound FCH with the low ammonia compound FCD, having the same *p*H but higher KOH content, shows the inadvisability of depending on high ammonia content instead of KOH to produce the desired *p*H. The low ammonia compound has a higher mechanical stability, and changes less on standing than the high ammonia compound with the same *p*H. The highest stability in the presence of high ammonia is obtained in compound FCI containing KOH approximately equal to the KOH number.

Data for the high ammonia compounds FDH, FDI, and FDJ, containing Captax, which are given in Table V, confirm the statements made above. Compound FDH, containing high ammonia and low KOH, coagulated in less than 16 hours, while compound FDA, containing the same amount of KOH, but with low ammonia, had not coagulated in spite of its low *p*H value.

The desirability of keeping the ammonia content low, even when the theoretical amount of KOH is added and the *p*H is between 10.5 and 11.0, is not fully apparent from the data given. However, it has been found in factory processing that if the ammonia is not reduced, the compounds gradually and continuously develop a fine grain coagulum which plugs strainers and seriously interferes with processing. Furthermore, even though the latex is strained, additional coagulum develops, which becomes progressively more difficult to remove.

It should also be mentioned that it is highly undesirable to add more formaldehyde than is required to reduce the ammonia content below 0.05-0.1 part per 100 parts of rubber for two reasons. First, the reaction of formaldehyde with ammonia is not an ionic reaction, but requires a finite period of time for completion. If sufficient formaldehyde is added to react with all of the ammonia, the compound thickens, due to agglomeration of the latex particles. Secondly, as mentioned previously, the rate of change of *p*H with KOH content decreases rapidly as the ammonia content is varied between 0.0 and 0.2 parts. Therefore, hydrolysis of compounding ingredients or slight errors in compounding produce less acute effects if the ammonia is not completely removed.

In the above discussion the ammonia content has been referred to the rubber content for convenience in compounding. It is obvious, of course, that from the standpoint of its effect on the solubility of zinc oxide, the concentration of the ammonia in water is important. Referred to the water, the ammonia should be reduced to a value between 0.12 and 0.22%. The permissible ammonia content on the rubber basis thus becomes greater as the total solids content of the compound is reduced.

4. *Effect on Total Solids Content.*

It has been found that the manner in which the mechanical stability varies with *p*H is independent of the total solids content between 20 and 58% T.S., and that the maximum stability is obtained when the compound has a *p*H of approximately 10.7. As is well known, the magnitude of the stability increases rapidly with dilution of the latex under constant conditions of *p*H and salt concentration. Therefore the *p*H limits between which a latex compound has a mechanical stability greater than a certain predetermined value widen very

rapidly with decrease in total solids content. This means that the tolerances in *p*H and KOH content, as well as in ammonia content, become greater as the total solids content is reduced. Compounds satisfactory for many practical purposes can be made at lower total solids (*e.g.*, 20-30%) without rigid adherence to the principles previously outlined, which define the conditions required for optimum properties.

5. *Effect of Vulcanization in the Latex State.*

Even though a compound is properly balanced in regard to *p*H and ammonia concentration, severe thickening due to prevulcanization may occur, particularly in warm weather, if the compound contains ultra-accelerators, although in general the stability is unaffected. Thickening of this type should, of course, not be confused with thickening produced by zinc oxide. The degree of vulcanization in a latex compound, if not too great, may be measured by determining the T-50 value of a film made from the compound, according to the procedure described by Gibbons, Gerke and Tingey[8]. Further data on this subject will be published at a later date.

SUMMARY AND CONCLUSIONS

1. From measurements of the cataphoretic mobility of latex particles in potassium and calcium buffers, respectively, it has been calculated that in order to obtain high stability in latex compounds, the concentration of divalent ions must be of the order of 0.002 *M* or less.

2. Measurements of the cataphoretic mobility of latex particles suspended in solutions of constant zinc and ammonia concentrations indicate that in the presence of dissolved zinc oxide the stability of latex is increased with increasing *p*H above *p*H 9.6. This is attributed to conversion of divalent zinc ammonia ion ($Zn(NH_3)_4^{++}$) into monovalent zinc ammonia hydroxide ion ($Zn(NH_3)_3OH^+$).

3. A consideration of the mass action equations for zinc hydroxide and zinc ammonia hydroxide shows that the concentration of divalent zinc ion decreases rapidly as the ammonia concentration is reduced or as the *p*H is increased.

4. The KOH number of latex is defined as the number of grams of KOH per 100 grams of rubber corresponding to the end point (at *p*H 10.7-11) in the electrometric titration of latex with KOH. Experimental precautions in determining the KOH number are discussed.

5. Data are given which show that the KOH number of a normal latex may be reduced more than tenfold by creaming three times from 33% T.S. to 62% T.S.

6. The KOH numbers of commercially available normal latices have been found to vary between 1.2 and 2.4, and those of creamed or centrifuged latices between 0.55 and 0.95.

7. The amount of KOH for optimum stabilization (*i.e.*, maximum stability, minimum viscosity and minimum change of properties with time) of zinc oxide compounds containing no added buffering ingredients varies with the latex, and is numerically equal to the KOH number. This quantity of KOH produces a *p*H of 10.7-11.0.

8. If appreciable amounts of protective ingredients such as casein, glue or gum arabic are added in compounding, sufficient additional KOH must be added to maintain a *p*H of 10.7-11 in the latex compound. The amounts of KOH required may be determined by electrometric titration of the protective ingredients.

9. Optimum stabilization in zinc oxide compounds containing Captax is ob-

tained at *p*H 10.5, when the amount of KOH added is equal to the KOH number of the latex plus two-thirds of the amount stoichiometrically equivalent to the Captax. Similar allowances for the alkali combining power of other acidic or hydrolyzable accelerators or compounding ingredients must be made.

10. It is shown that the stability of zinc oxide compounds at a given *p*H is increased if the ammonia content is reduced. The optimum ammonia content has been found to be between 0.12 and 0.22% of the water content.

The writer records his indebtedness to B. W. Bender, P. D. Brass, E. Hazell, C. P. Roe, S. I. Strickhouser and W. A. Gibbons, Director of Development, for many helpful suggestions and constructive criticisms.

REFERENCES

[1] It has been found in these laboratories that quantitative agreement is obtained in the mobility-pH curves for quartz particles suspended in solutions of latex protein and for highly diluted latex, respectively. These experiments confirm a similar conclusion by Kemp and Twiss, *Trans. Faraday Soc.* **32**, 890 (1936).
[2] Abramson, "Electrokinetic Phenomena", New York, **1934**.
[3] It should be pointed out that this low mobility cannot be accounted for by the increase in ionic strength to 0.4, due to NH_4Cl.
[4] For Equations 2 and 3, see Kolthoff and Kameda, *J. Am. Chem. Soc.* **53**, 832 (1931).
[5] McGavack and Rumbold, *Ind. Eng. Chem., Anal. Ed.* **3**, 94 (1931).
[6] The end point of the titration curve is unaffected by the presence of hexamethylenetetramine thus formed, as this chemical does not buffer between pH 6 and pH 11
[7] Jordan, Brass and Roe, *Ind. Eng. Chem., Anal. Ed.* **9**, 182 (1937).
[8] Gibbons, Gerke and Tingey, *Ind. Eng. Chem., Anal. Ed.* **5**, 279 (1933).

NOTE ON THE EXTRACTION OF RAW RUBBER WITH ACETONE *

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INTRODUCTION

The progressive extraction of sulfur from vulcanized rubber has been studied in great detail, but less attention has been given to the progress extraction of raw rubber with acetone. In the course of other work we had occasion to extract exhaustively some specimens of rubber, and the anomalous results induced us to go further into the matter. It was suspected that acetone-soluble oxidation products of rubber were being formed. This paper is a result of such further investigation.

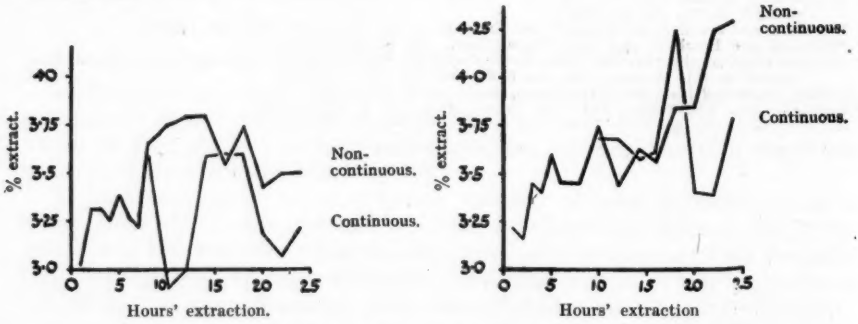

Fig. 1.—Acetone extracts of raw rubber; plotted from data of Endo.[9]

In "Rubber, Physical and Chemical Properties," **1935**, p. 532, Dawson and Porritt recommend the following precautions in the case of raw rubber: "Rubber should be sheeted out very thinly on a cold mill, . . . and wrapped in extracted linen; there is no need to use a paper extraction thimble in this case. . . . Extract for at least 7 hours. . . . The extraction should be continuous, as interruption for any length of time may lead to oxidation of the rubber, and hence an incorrect result, unless the rubber is left covered with acetone." These authorities therefore recognize the risk of oxidation, but the only precaution recommended to prevent it is exclusion of oxygen by covering the rubber with acetone while it is not being extracted.

There seem to be differences of opinion in the literature as to the time of extraction necessary and the details of the method of extraction. Zilchert[1] states that 10 hours' extraction on a steam-bath is usually sufficient to give results sufficiently accurate for commercial purposes. Spence and Scott[2] state that the extraction of resins from rubber is an exceedingly slow process. Lagerquist[3] states that independent determinations of the acetone-soluble substances in rubber frequently show considerable discrepancies. Whitby and Winn[4] extracted rubber for 48 hours in a special apparatus. Henri[5] showed that ultra-violet rays

* Reprinted from the Proceedings of the Rubber Technology Conference, held under the Auspices of the Institution of the Rubber Industry, London, May 23-25, 1938. Paper No. 8, pages 281-286.

activate greatly the atmospheric oxidation of rubber. Asano[6] found that light assists oxidation of rubber and increases the acetone extract. Dufraisse and Drisch[7] measured the rate of oxygen absorption by rubber and showed that the return of the acetone extract to extracted crepe caused a large reduction in oxidizability. Bondy and Lauer[8] showed that the antioxidant present in latex is effective only in the solid state and that oxidation only occurs in light.

Endo[9] has carried out very detailed investigations into the acetone extraction of raw rubber. Pale crepe from one shipment was cut into sheets of about 1.6 to 2 grams, and one of these was used at a time for determining the amount and properties of the acetone extract and its variation under different conditions. Unfortunately this method of sampling does not ensure uniformity, so that the amount of extract, for example, does not increase steadily with time, due no doubt to the sample pieces not being all of the same composition. If, however, his results are plotted it will be seen (Fig. 1) that a large amount of the extract is removed in the first 1 or 2 hours, but that subsequently there appears to be on the average a slow rise. He does not appear to have taken any special precautions to exclude light.

EXPERIMENTAL

We found that definite values for acetone extract could not be obtained when the rubber was extracted in an apparatus of the A.S.T.M. type, the rubber being

TABLE I

% acetone extract					
In light (winter daylight, London)			In darkness		
Hours' extraction	Crepe	Whole rubber	Hours' extraction	Crepe	Whole rubber
18	3.01	7.66	6	2.75	6.05
36	3.26	8.32	14	3.17	6.96
54	3.74	8.58	22	3.17	7.06
72	3.97	9.25	30	3.17	7.06

rolled between filter paper and with the extractor standing in the light, that is, in front of a window. The extracts were dried to constant weight at 70° C. The experiments were made in January and February of this year, and there was very little direct sunlight, but mainly diffused light such as is usually experienced in London in the winter months. After an initial rapid extraction the extract continued to rise slowly, without showing any signs of reaching a constant value. Extractions were therefore made with the following precautions: The rubber was completely wrapped in a roll of filter paper and the roll covered at both ends with filter paper; the extractor was kept in a dark corner and shielded from light; the thimbles were kept full of acetone and in the dark whenever the extraction was not in progress. The extraction was not, of course, continuous, being interrupted at nights and while drying down to weigh the extract. The figures obtained are given in Table I and compared with those obtained in the light.

In the dark the extract soon reaches a constant value, but in the light it rises continuously without showing any sign of reaching a maximum figure. The results are illustrated in Fig. 2.

The specimens which had been extracted in the dark were now exposed to diffused daylight for a day and then re-extracted for 8 hours in the dark. The following further extracts were obtained:

From crepe 0.21%
From whole rubber..... 0.02%

Exposure to light evidently caused some oxidation in the crepe. Presumably there was sufficient antioxidant left in the whole rubber to prevent oxidation. After this extraction the specimens were kept in the dark for two days, but with free access of air, and were again extracted in the dark for 8 hours. There was no extract from either the crepe or whole rubber. It therefore appears that exclusion of light is more important than partial exclusion of air.

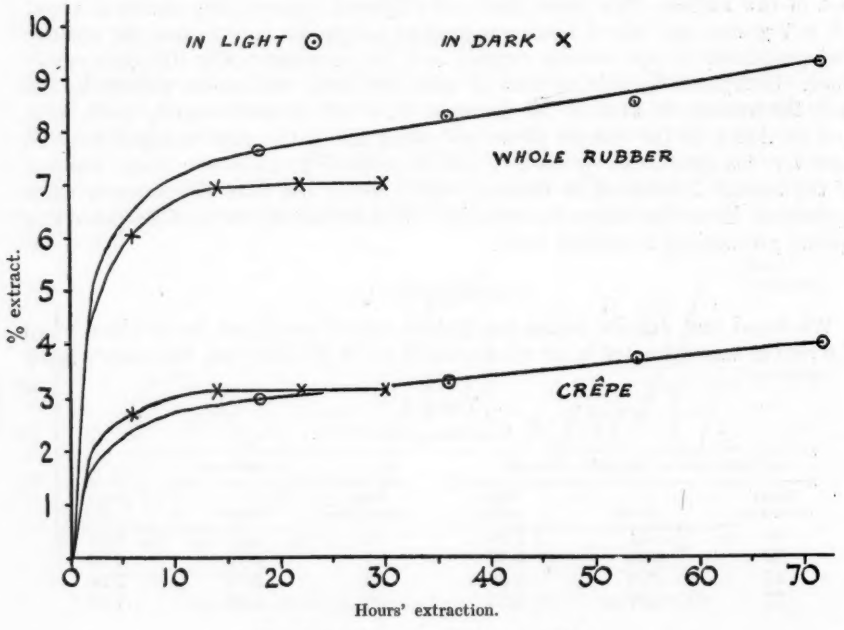

FIG. 2.—Acetone extracts of raw rubber.

It was thought that if the specimens were completely wrapped in filter paper in the thimbles, the exclusion of light would be sufficient without screening the extractor. The extractor was therefore replaced in front of the window, and one sample each of the crepe and whole rubber was partially exposed by removing part of the filter paper while another sample of each was kept completely wrapped. They were then extracted for two days.

	Partly exposed		Wrapped in filter paper	
	Crepe	Whole rubber	Crepe	Whole rubber
Extract	0.33%	0.48%	0.26%	0.12%

The partly exposed specimens have oxidized more than the completely wrapped ones, but complete wrapping has not been sufficient to prevent oxidation entirely. The above experiments were made on rubbers prepared in the laboratory from ammonia-preserved latex. In order to check the results on rubbers from fresh latex two commercial rubbers were used, a Ceylon blanket crepe and a F.M.S. smoked sheet. They were milled out thinly on cold rolls and wrapped in strips of filter paper. The extractor was stood in a dark corner and shielded from

light. During interruptions of extraction the thimbles were kept in the dark. The results obtained are shown in Table II and illustrated graphically in Fig. 3. Extraction is substantially completed in 18 hours.

TABLE II

Hours' extraction	% acetone extract in dark	
	Blanket crepe	Smoked sheet
4	3.10	2.97
10	3.28	3.22
14	3.33	3.29
18	3.39	3.29
25	3.39	3.29

TABLE III

Hours' extraction	% acetone extract					
	Blanket crepe			Smoked sheet		
	In dark	Completely wrapped	Partly wrapped	In dark	Completely wrapped	Partly wrapped
10	3.28	3.21	3.38	3.22	3.22	3.58
18	3.39	3.42	3.61	3.29	3.88	3.86

The rising acetone extracts obtained in the light (Table I and Fig. 2) were obtained on rubbers which had been nearly completely extracted, and might, therefore, be exceptionally sensitive to oxidation. Further samples of the same pieces of milled blanket crepe and smoked sheet were therefore extracted in the

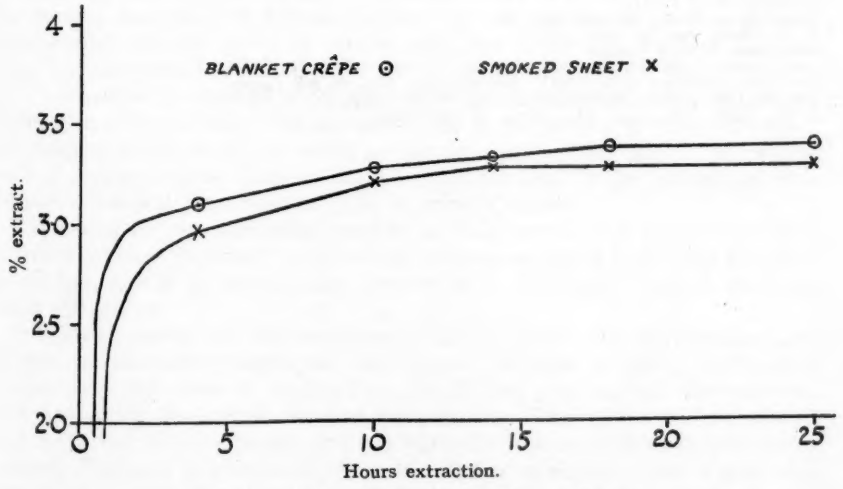

FIG. 3.—Acetone extraction of raw rubbers in the dark.

light. One piece of each was completely wrapped in filter paper and one piece of each was only partly wrapped. The results are given in Table III, together with the corresponding results obtained in the dark.

Complete wrapping of these rubbers prevented any effect by light in the early stages of extraction. Partial exposure however increased the extract to an amount greater than the final value obtained in the dark.

CONCLUSION

We have shown that if raw rubbers are exposed to light during acetone extraction, the extract does not reach a steady value but continues to increase slowly with time of extraction. If extraction is carried out in the dark, constant values for the extract are obtained after about 15 to 20 hours' extraction. In the same time the values obtained in the light are about 10% higher than the true values, obtained in the dark. If, however, in an attempt to obtain constant values, the extraction in light is continued for 70 hours, values are obtained about 25% in excess of the true ones. If, therefore, accurate values for acetone extract of raw rubber are required, extraction must be carried out in the dark until a constant value is reached. If, for convenience, light is not carefully excluded, it would appear that a comparatively short extraction, *e.g.*, 5 to 6 hours, would give the best results, since over 90% extraction is obtainable in 4 hours (Table II), and oxidation is not likely to be considerable in this period. In any case, shielding from direct sunlight is advisable.

In view of the general trend of the curves for acetone extract obtained by Endo[9], it is probable that oxidation of the rubber occurred, and that his results, particularly for the longer periods of extraction, are complicated by the presence of rubber oxidation products.

This work has been carried out on behalf of the Rubber Producers' Research Association, to whom the authors are indebted for permission to publish this paper.

REFERENCES

[1] *Gummi-Ztg.* **25**, 716 (1911).
[2] *Kolloid-Z.* **9**, 83 (1911).
[3] *Svensk Kem. Tidskr.* **33**, 198 (1921).
[4] *J. Soc. Chem. Ind.* **41**, 336T (1923).
[5] *Caoutchouc* **7**, 4371 (1910).
[6] *India-Rubber J.* **70**, 307 (1925).
[7] *Rev. gén. caoutchouc* **8**, 9 (1931); *Rubber Chem. Tech.* **5**, 301 (1932).
[8] *Ber.* **66**, 1611 (1933); *Rubber Chem. Tech.* **7**, 23 (1934).
[9] *J. Soc. Chem. Ind., Japan* **38**, (1935); **9**, 308 (1936).

IMPROVEMENTS IN METHODS FOR THE RAPID ANALYSIS OF RUBBER *

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In the course of experiments carried out by the research laboratory of the Compagnie du Gaz of Paris on rubber gaskets for gas lines, we were led to search for a more precise method for the determination of ingredients in vulcanized rubber which would be more rapid than the method involving mild incineration in a crucible.

When it is desired to make a rapid determination of the inorganic and organic substances in rubber, it is customary to incinerate the rubber in a closed crucible under moderate conditions. Although this method is rapid, it is not possible to separate with any degree of certainty the rubber from carbon black and mineral substances, for the rubber may carbonize in the crucible and leave a deposit of black, which adds itself to the black originally in the rubber and thus vitiates the results.

It was felt that incineration in an inert medium would give results which would approach more closely to the true values. Since in this case a crucible could not be utilized satisfactorily, recourse was had to a Pyrex tube containing a platinum boat. The apparatus finally adopted is described in the following pages.

However, before proceeding to describe this apparatus, we should like to call the reader's attention to a similar apparatus employed by M. Pellié, chemist of the Société Anonyme de Pont-à-Mousson, for the distillation of volatile substances and occluded gases in rubber after the latter has remained in pipe lines. In the method of Pellié, a current of carbon dioxide at a temperature of 80° C. is passed for several hours over shavings of rubber in a porcelain boat, confined in a Pyrex tube. Volatile substances in the rubber are thus entrained, and tend to condense at the outlet of the apparatus. The aim of the present work is obviously quite different, and the apparatus used by the present author is distinctly different from that of Pellié in certain respects.

The reason for mentioning the method of Pellié is that it is a good procedure to follow when it is desired to determine substances which have been absorbed by rubber, and is in certain cases preferable to the classic method involving steam distillation.

In analyses carried out by the present author, a Pyrex tube 500 mm. long and 40 mm. in diameter is employed. One end of the tube is drawn out, while a section near the center is flattened on the bottom part to hold the platinum boat containing the rubber cut into fine particles. The rubber is first washed with a current of hot nitrogen, and not until this is done is direct heating commenced. Nitrogen is introduced through a sort of sprinkler made of glass and then through a diaphragm composed of glass wool held between two discs of copper gauze, so that the sweeping action of the inert gas is distributed over the diameter of the tube. This uniform distribution is very important, for if nitrogen is introduced through a single tubule, eddy currents are set up in the tube, one disadvantage of which is that particles of black and mineral matter are entrained and the results are thereby vitiated hopelessly.

* Translated for Rubber Chemistry and Technology from the Documentation Scientifique (Revue Bimestrielle des Laboratoires et de l'Industrie Chimique) Vol. 7, No. 65, pages 179-181, September-October 1938.

After the platinum boat is placed in the tube, the diaphragm is placed in position and the tube is closed. All air in the system is then swept out for about one minute. The tube is then heated gradually, the first of the gas burners being lighted to heat only the nitrogen; following this the rubber in the boat is very slowly heated by lighting the second burner. This procedure is necessary to avoid blistering of the rubber, in which case expulsion from the boat may take place, thereby spoiling the test. If the operations are properly carried out, all organic substances and sulfur distil slowly and completely, and there is no carbonization. Heating is stopped when smoke is no longer evolved and when the residue in the platinum boat commences to turn reddish; the temperature inside the boat is then close to 500° C. The thermometer which passes into the tube through the tubule, and the bulb of which touches the wall of the platinum boat, indicates a temperature in the neighborhood of 430° C. This difference in temperature is due to the current of nitrogen, which cools the thermometer slightly.

The boat is allowed to cool in the current of nitrogen. The difference between the weight of the capsule containing the rubber and the new weight after heating represents the quantity of organic substances distilled away. After weighing, the contents of the platinum boat are calcined at a dull red heat, in an oxidizing atmosphere, until all black is burned away. After cooling, a new weighing is made, and the difference between this weight and the previous weight represents the quantity of black burned away. The residue is the quantity of mineral substances contained in the original sample.

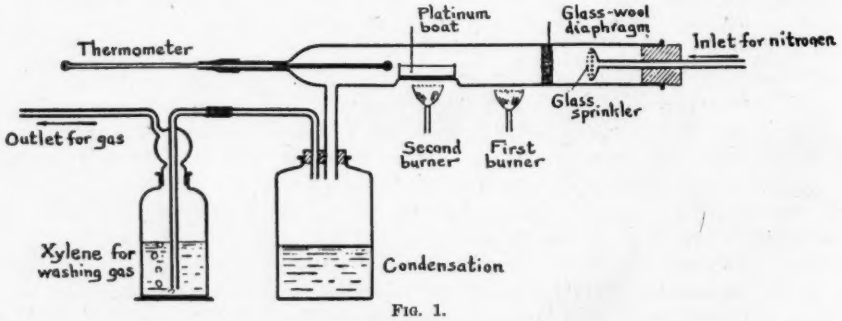

FIG. 1.

From the outlet of the tube, the vapors from the rubber which are entrained by the current of nitrogen are bubbled into a Durand bottle half-filled with xylene, in which the greater part of the vapors condense. The function of this bottle is primarily to indicate the rate at which the current of nitrogen is passed through the system, and also to prevent contamination of the outside atmosphere with vapors formed by the pyrogenic decomposition of the rubber.

Part of the distillate from the rubber condenses also in the cold part of the distillation tube itself, and flows through the lower tubule on the wall of the distillation tube, into the first condensation bottle.

Fig. 1 shows in the simplest possible way the assembly of the apparatus.

The time required for a complete determination, including precise weighings, is not over 40 minutes. This method is therefore almost as rapid as the mild incineration method in a closed crucible, and it gives more accurate results without involving any difficulties.

COLOR MEASUREMENT AND ITS APPLICATION IN THE RUBBER INDUSTRY *

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INTRODUCTION

The object of this paper is to bring to the notice of rubber technologists the recent advances which have been made in the science of color measurement and its applications.

As the demand for colored articles increases, it becomes necessary to use a more specific way of recording color than to say that an article is "rose pink" or "olive green." The use of standard samples is cumbersome in regard to storage, and may be misleading in the case of rubber products, as they are liable to color changes.

The increasing use of raw rubber in the form of latex has raised the question of the measurement of its "whiteness" as a guide to its quality. It has been suggested also that the transparency of thin dried latex films could be used for this purpose. Both these methods entail the measurement of the color of almost white objects.

MacAdam[1] has shown that it is difficult to judge the whiteness of articles by direct vision. He asked 30 observers, half of whom were women, to arrange white objects in order of increasing whiteness. The arrangements showed great divergence, and the observers were unable to repeat their observations. When these samples were classified by means of a suitable colorimeter, consistent and reproducible results were obtained by different observers.

Visual observations are subject to the effect of many variables, and are therefore so misleading that it at once becomes apparent that such determinations can only be successfully carried out with a colorimeter used under carefully standardized conditions.

Besides the measurement of the whiteness of latex such problems arise as the covering power of pigments, especially of white pigments, the use of dyestuffs in brightly colored articles, the transparency of rubber lacquers and varnishes, all of which require a measurement of color in some form or another.

COLOR

Color is a general name applied to all sensations arising from the activity of the retina of the eye and its attached nervous mechanisms, this activity being, in nearly every case, a specific response to radiant energy of certain wavelengths and intensities.

It has been known for a long time that the sensation of color is jointly due to properties of the object, the illumination and the eye. It is only in recent years, however, that the true physical relationship between these three factors has been fully appreciated. As a result, color measurement has been transformed into an exact science, and it is now possible to express color in numbers as definite as those used for size and weight.

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In order to measure the color of a body, light from three standard sources of different colors is mixed in such proportions that the additive effect gives the same sensation of color to the eye as that from the object. It should be realized that a body which appears, for example, green does not necessarily reflect light of wave length corresponding to the green part of the spectrum. The green sensation may be due to the additive effect of lights of other wave lengths, so that bodies which appear to be the same in color may be reflecting quite different groups of wave lengths. The process of mixing light from colored sources must not be confused with that of mixing pigments. In the latter case each pigment absorbs a characteristic and definite portion of the incident light, irrespective of the other pigments present, with the result that the color of the mixture is due to the residual reflected portion which reaches the eye.

THE ATTRIBUTES OF COLOR

Any color can be specified in terms of three fundamental attributes, without reference to the stimuli which give rise to the color sensation. These attributes are:

(i) Brightness or luminosity, which specifies the amount of light reflected or transmitted by the spectrum.

(ii) Hue, which is the measure of the difference between a color and a gray of the same brightness, giving it the character of being reddish, yellowish or the like.

(iii) Saturation, which measures the amount of hue present.

WHITENESS

In a strict sense, there is no difference between white and color, white really being the color of a body which is incapable of any marked absorption or selective reflection. In this sense, white is a particular color and there is no "degree of whiteness." However, custom has led to the classification of all colors which are almost white under the heading "white," and the degree by which they differ from absolute white is measured by what is termed their whiteness.

TRICHROMATIC REPRESENTATION

Experiment has shown that most colors can be matched by mixing red, blue and green lights in the correct proportion.

The result of any such matching can be expressed in terms of the proportion of each of the unitary stimuli used and is written:

$$C = rR + gG + bB,$$

where C is the color, R, G and B represent the unitary stimuli, and r, g and b are coefficients expressing the proportions of the unitary stimuli. It has been found to be convenient to choose units such that:

$$r + g + b = 1. \qquad (1)$$

But R, G and B are arbitary unitary stimuli, and the units in which these quantities are expressed have also been arranged so that equal quantities of each are required to match a standard white, hence:

$$W \text{ (standard white)} = \tfrac{1}{3}R + \tfrac{1}{3}G + \tfrac{1}{3}B. \qquad (2)$$

Equations (1) and (2) completely specify the system. From equation (1) it follows that color can be expressed in terms of any two of the three coefficients.

Two objects with the same values of r, g and b will, when brought to the same

brightness, have the same color. A color can therefore be completely specified in terms of two coefficients and a brightness factor, all of which can be measured on a standard colorimeter, without reference to the original stimuli which give rise to the particular sensation of color in question.

It should be noted that the unitary stimuli are arbitrarily selected and are not pure colors. The green and blue units, for example, both contain some red. Thus it may prove impossible, in the case of saturated spectral colors, to obtain a match. A mixture of the green and blue units, as it were, requires some of the red subtracting, giving a result such as:

$$C = -r\mathrm{R} + g\mathrm{G} + b\mathrm{B}.$$

Such colors are measured by diluting them with a known amount of white light or of a suitable one of the unitary colors, and measuring the color of the mixture.

The Commission Internationale de l'Eclairage in 1931 recommended the adoption of a new set of hypothetical unitary stimuli which make it possible to represent all colors wholly by positive coefficients[2]. The conversion of results from one set of unitary stimuli to another involves only a relatively simple calculation, details of which have been given in several papers[3].

ILLUMINATION

The color of an object depends in part on the illumination; a white object will appear red in red light, for example. It follows that for accurate colorimetry a standard source of light is essential. This must have both constant intensity and standard distribution of energy between the different wave lengths. Daylight does not satisfy these conditions. The carbon arc gives a strong light of about the correct color, but it is liable to fluctuate more than 200° C. in temperature.

An ordinary electric lamp has a high intensity, does not vary if the voltage is constant, and reproduces the same color over a considerable length of its useful life for a constant voltage. Unfortunately no two lamps give light of the same color for a given applied voltage. To overcome this difficulty the C.I.E. has specified the "color temperature" at which gas-filled lamps should be operated, that is, the temperature to which a theoretical "black body" must be raised to cause it to emit light of the same nature as the lamp[2].

At the same time two liquid filters were described, which, when used in conjunction with the standard lamp, give a light which resembles daylight.

To be able to ensure that a lamp is being operated at the correct color temperature, it should be calibrated by some standardizing laboratory, such as the National Physical Laboratory or the U.S. National Bureau of Standards, before being put into use.

To avoid difficulties with glossy surfaces, it is standard practice to illuminate all surfaces at an angle of 45° and take observations along a normal.

As a standard of whiteness the C.I.E. has defined a film of magnesium carbonate or oxide in the pure state.

EFFECTS OF VISION ON COLORIMETRY

Ultimately, whatever apparatus is used, matching or final measurement has to be made. For this must be used either a photoelectric cell or the eye. The photoelectric cell is the more sensitive, but in general its response is different from that of the eye, and the cell is not as reliable as the eye for general measurement.

Account has thus to be taken of various defects of vision which affect color

measurements. They fall into two classes, abnormal response to change in intensity and abnormal sensitivity to change in color.

Variation in Response over the Retina.—The sensitivity of the eye to changes of brightness varies according to the part of the retina on which the light falls. Also, the fovea is more sensitive to red than the peripheral region and, owing to the large area of the latter, bluish shades tend to be enhanced.

As the intensity of the spectrum is reduced the part which appears brightest seems to move towards the ultraviolet end of the spectrum, though this effect, the Purkinje effect, is not appreciable with most persons if the light is confined to the fovea.

Field Size.—It will be realized that if light falls only on the fovea, some defects of the eye are minimized, and to this end the C.I.E. has adopted a standard circular field of diameter 2° for use in colorimetry.

Chromatic Properties of the Eye.—Sensitivity to changes of intensity in the blue and yellow regions of the spectrum is small and the response to these colors varies among different persons. While these colors contribute little to brightness, however, experiment has shown that there is a sharp maximum in the response curve in the blue region.

The length of the spectrum visible to different persons varies, and any shortening at the blue end will affect the response and hence the ability to differentiate between colors.

When a colorimeter is used these defects can be allowed for, providing they are not very marked. To establish a standard of reference, the C.I.E. has defined a hypothetical standard observer based on results of Guild[4] and Wright[5].

APPLICATION OF PHOTOELECTRIC CELLS

The response of photoelectric cells is too variable to make them suitable alternatives to the eye except in special colorimeters. The response of a given cell varies with the position of the light on the plate and the time of exposure to the light. Such cells, however, have been used successfully in apparatus designed to measure whiteness.

In selecting a cell for this purpose, choice must not be based on the response of the cell to the equal-energy spectrum, which is the usual response curve supplied with the cell. The standard colorimetric sources do not emit equal-energy spectra.

COLORIMETERS

The earliest attempts to classify color were by means of color albums or dictionaries, consisting of slips of colored material arranged in some order of hue and saturation. Examples of such albumns are Ostwald's *Farbenatlas,* and the Dictionary of Color published by Maerz and Paul in 1922, which contains 7000 colors.

THE LOVIBOND COLORIMETER

The simplest type of colorimeter to use is the subtractive one, a typical example of which is the Lovibond Tintometer. In this instrument graded filters of increasing depth of red, yellow and blue are placed in the path of light from a special daylight lamp, until the transmitted beam is of the same color and intensity as the light from the specimen. The filters are numbered according to their intensity and as the scale is arbitrary the color is given in "Lovibond Units."

The instrument is not a precision one and is designed essentially for factory control, where a rapid comparison of colors is required. However, if proper precautions are taken, there seems to be no reason why this instrument should not

be used for accurate work, especially if the individual filters are calibrated, and provided that a standard source of illumination is used.

The instrument is, however, unsuited for the measurement of the color of nearly white samples as the steps between the filters are too great.

THE DONALDSON COLORIMETER [6]

This instrument is a trichromatic colorimeter, which measures color in terms of three standard stimuli or primaries.

The light from a lamp passes through three rectangular apertures covered with the three colored filters, and is then focussed by a lens into the inside of an integrating sphere. The rays are thoroughly mixed inside this chamber by multiple reflection, and a beam of uniform light emerges from the outlet aperture. This beam then passes into the telescope, where it is viewed side by side with the light reflected from the sample. The three rectangular apertures are provided with sliding shutters which are adjusted so that the color and intensity of the synthesized light matches that reflected from the sample. The color of the sample is deduced from the settings of these shutters. The instrument is fitted also with means for desaturating highly saturated colors so that it can be used for spectral hues.

It is a precision instrument, which can be used to measure colors accurately in terms of the C.I.E. scale. It can be used satisfactorily to measure the color of nearly white samples, its sensitivity being limited only by that of the human eye.

THE BLANCOMETER [7]

Mention has already been made of the use of photoelectric cells in the measurement of whiteness. The Blancometer is an instrument of this type.

Light reflected from a standard white screen (magnesium oxide) is adjusted by movable neutral-tint wedges until it has the same intensity as the light reflected from the sample. The position of the wedges thus gives a measure of the reflecting power of the sample. The intensity of the light reflected is measured by means of a photoelectric cell connected to a sensitive Lindemann electrometer. Tests are made successively with red, green and blue filters imposed in the path of the beam of light. In the normal Blancometer the readings cannot be converted into values on the C.I.E. color scale, but a modified model is now available which enables this to be done.

There are many instruments of the same types as the above, some of which are similar in principle and quite as accurate.

An instrument somewhat similar in principle to the Blancometer has been described by Williams[8], and is known as the Bolton and Williams Photoelectric Colorimeter. In this instrument the percentage of light reflected by the sample is compared with that reflected by magnesium oxide.

MEASUREMENTS OF THE WHITENESS OF LATEX

The following experiments were carried out by the Research Association of British Rubber Manufacturers in order to ascertain a type of colorimeter satisfactory for the measurement of the whiteness of latex. From time to time suggestions have been put forward for the design of simple inexpensive instruments for this purpose. However, it will be apparent that so many conditions have to be satisfied in such a design, that any such simple device cannot be successful.

In this investigation five normal (38-40%) latices, some of which were "off color," were examined by four observers, who were asked to arrange them in order of whiteness. The experiments were carried out in a room with buff walls and a white ceiling, on a day when the sky was overcast, in order to obtain as neutral a light as possible. The latices were well shaken up and poured into flat dishes. One observer (I) arranged the samples on two different occasions. The results are given in the following table, where the letters denote the latices.

The samples C and E were much darker than the others, and have been placed in the same position by all observers. Apart from these two, the observers have placed the other three latices in different orders, and there is no agreement between the two attempts by the first observer. Indeed, the five arrangements of the samples B, G, and H show no more agreement among themselves than 5 random selections. These observations are in agreement with the work of MacAdam.[9]

	Observer				
	I(*a*)	I(*b*)	II	III	IV
Whitest	B	B	H	G	G
	G	H	B	H	B
	H	G	G	B	H
	C	C	C	C	C
Darkest	E	E	E	E	E

Arrangements were made to have these latices examined by the Lovibond Tintometer, the Donaldson Colorimeter and the Blancometer.

It was found impossible to obtain a true match on the Lovibond Tintometer, as the gradation of the filters was too steep. It was decided to discontinue these measurements.

The following results were obtained on the Donaldson Colorimeter with C.I.E. Illuminant B, and are expressed in terms of the reflection from the magnesium oxide screen (100%).

	% of light through each filter			Total light
Sample	Red	Green	Blue	R+B+G
B	16.0	36.0	34.6	86.0
C	16.1	31.6	34.0	81.7
E	14.0	29.0	33.7	76.7
G	16.0	36.0	36.0	88.0
H	17.0	33.0	35.0	85.0
MgO	20.5	40.0	39.5	100.0

It will be seen that when compared with magnesium oxide, the samples are gray, the lightest reflecting 12% less light and the darkest 23.3% less. The samples B, G and H are easily separated, and the samples are arranged in the following order: G, B, H, C and E.

With the Blancometer similar results were obtained, as will be seen from the following table.

	% reflection with each filter		
Sample	Red	Green	Blue
B	77.8	76.0	71.0
C	69.6	69.4	66.6
E	56.4	56.4	56.1
G	79.5	77.1	69.1
H	76.0	75.3	70.3

This instrument also arranges the samples in the following order of whiteness: G, B, H, C and E.

Between the lightest and darkest samples it can be shown that about 150 colors could be detected by the eye with the aid of a suitable colorimeter. The Donaldson Colorimeter is capable of this accuracy. On the other hand, the Blancometer is capable of this accuracy. On the other hand, the Blancometer is independent of the eye and, as the photocell is more sensitive, this instrument will distinguish over a thousand colors in this range.

It will therefore be seen that, while colorimeters will accurately grade samples in order of their whiteness, there is a marked disagreement among visual observations. In fact, any method which relies on the unaided eye will be influenced to a greater or less extent by the conditions of observation and the vision of the observer.

In order to obtain a reasonably accurate measure of color a colorimeter of some type is required and, when white samples are being dealt with, it should preferably be of the trichromatic or Blancometer type.

The writer wishes to thank the Board of Management of the Research Association of British Rubber Manufacturers for permission to publish this paper.

REFERENCES

[1] *J. Optical Soc. Am.* **24**, 781 (1934).
[2] *Trans. Optical Soc.* **33**, 73 (1931-32).
[3] See Ives, *J. Franklin Inst.* **195**, 23 (1923); Guild, *Trans. Optical Soc.* **26**, 95, 139 (1924-25); Froelich, *J. Optical Soc. Am.* **9**, 31 (1924); Priest, Tuckermann, Ives and Harris, *J. Optical Soc. Am.* **9**, 503 (1933); Bouma and Haler, *Proc. Acad. Sci. Amsterdam* **38**, 258 (1936); Holmes, *Proc. Phys. Soc.* (London) **37**, 400 (1935).
[4] *Trans. Roy. Soc.*, London **230A**, 149 (1931).
[5] *Trans. Optical Soc.* **30**, 141 (1928-29).
[6] Donaldson, *Proc. Phys. Soc.* **49**, 6, 1068 (1935).
[7] Charters, *J. Soc. Dyers Colourists* **48**, 160 (1932); Adam Hilger, London **1931**.
[8] *Analyst* **62**, 3 (1937).
[9] *J. Optical Soc. Am.* **24**, 781 (1934).

AN INVESTIGATION OF THE PERFORMANCE OF FLAT AND V-TYPE TRANSMISSION BELTS *

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INTRODUCTION

A major problem in engineering is and always will be the efficient and effective transmission and distribution of motive power. In spite of the extensive developments which have taken place in individual direct, gear or chain coupled drives, there still remains an extremely large number of drives installed or being installed for the transmission of power in which belting of one kind or another is preferable. Such drives also vary tremendously in character and type, from small machines requiring a fraction of one horse power, to heavy industrial drives, as those used in rolling mills, where the power transmitted often extends to several hundred horse power. The nature of the load may be smooth and uniform or subject to heavy peak loads such as occur in the case of ore crushers or pumping machinery.

The use of belting for the transmission of power actually dates almost from the time that mechanical power began to be used, and in fact the name of Leonardo da Vinci has been mentioned as one of the first to devote attention to the fundamental principles of belt drives as well as being the inventor of the tension or jockey pulley. In spite of this, however, very little development in what may be termed the technology of belting appears to have taken place until the latter part of the nineteenth century and, as may be anticipated, most of the earlier writers gave special attention to the question of leather belting.

From a brief survey of the early literature on the subject, the first treatise on belting technique would appear to have been published by Moll and Reuleaux in 1853 under the title of "Der Konstrukteur," while several publications between the years 1868 and 1878 dealt with the fundamental mechanics of belt action, particularly with regard to the phenomena of creep and slip and the static frictional properties of belting. In 1894, experiments carried out with the object of measuring the efficiency of belt and rope drives were reported to the Institution of Mechanical Engineers, while a certain amount of practical engineering data on belting was published by F. W. Taylor in the same year.

With the turn of the century, published works became more numerous and the nature of the work more fundamental. A considerable amount of work, for example, was carried out by Fieber and Kammerer in Germany on the efficiency of belts and the centrifugal effects obtained with speeds up to 7,000 feet per minute. Measurements of the frictional properties of leather belting were also made by Friedrich in 1915, and in 1925 C. A. Norman measured the tension ratio and the transmissive features of various belts by means of a static slip machine.

Later on, various forms of dynamometer tests were developed and an investigation of belt creep in open, crossed, horizontal and vertical drives was reported by R. F. Jones[1], who used leather belting and found that more power was trans-

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mitted when the grain side of the belt was run next to the pulley. He also found that a leather belt in good condition transmitted its maximum power at speeds between 7,000 and 8,000 feet per minute. A handbook published by J. Dawson, Jr.[2], in 1930 gave test data on the mechanical efficiency of belt and rope drives, which were obtained on a dynamometer in which the power losses were measured electrically. These results showed that with a belt speed slightly in excess of 4,300 feet per minute, efficiencies of the following order were obtained:

Type of drive	Efficiency
Balata, V shaped rope	96.3%
Cotton rope (round)	92.9%
Leather belt	97.1%
Balata belt	97.8%

A year later Norman and Moffatt[3] published dynamometer tests on flat belting, including leather, stitched canvas, solid woven cotton, hair, and rubber and canvas belting.

In all these investigations the dynamometers used worked on either the Hopkinson regenerative principle, where the output of the generator was fed back direct into the motor with a suitable voltage control, or the generator output was fed back directly into the d.c. mains, again with suitable voltage control.

In 1928, however, an investigation of the fundamentals of power transmission by belts was published by Swift[4], in which a machine embodying a closed mechanical energy circuit was used and this was obtained by the employment of a secondary belt drive and a pulley of adjustable diameter. This comprehensive survey, which was carried out at Bradford Technical College, included measurements of the performance characteristics of leather, leather-cotton, woven cotton, woven hair, balata and rubber-canvas belting.

The following figures for the "coefficient of performance" or "pull efficiency," $\left(\frac{T_1 - T_2}{T_1}\right)$, for different types of belting, obtained under conditions of constant tension between the pulleys, can be quoted from this paper. The figures represent the coefficient of performance obtained when maximum power was being transmitted.

Belt	Mean tension 100 lbs.	Mean tension 200 lbs.
Leather, dressed—		
Hair side to pulley	0.97	0.96
Flesh side to pulley	0.90	0.87
Leather, undressed—		
Hair side to pulley	0.96	0.90
Flesh side to pulley	0.85	0.86
Woven cotton	0.92	0.89
Woven hair	0.71 to 0.89	0.70 to 0.87
Balata-canvas	0.68	0.73
Rubber-canvas	0.85	0.82
Leather-cotton compound	0.95	0.94

In the same year, two other workers published details of typical electrical machines which were used for measuring the performance characteristics of rubber and canvas belting, or as it is more generally termed, rubber transmission belting. In one case, Sturtevant[5] used a 100 h.p. Sprague electric dynamometer and a typical 4-inch × 4-ply rubber belt running on 24-inch pulleys at approximately 3,000 feet per minute and with a total tension of 480 lbs. He

found that under these conditions approximately 30-35 h.p. could be transmitted before the slip exceeded 1%, and that the coefficient of performance $\left(\frac{T_1-T_2}{T_1}\right)$ obtained with a high-grade belt was 88.5%. The equipment used by Sturtevant consisted of a motor and a generator, the latter being movable and provided with apparatus for measuring the total belt tension, whilst each machine was cradled and connected to a Toledo scale for the measurement of the torque reaction.

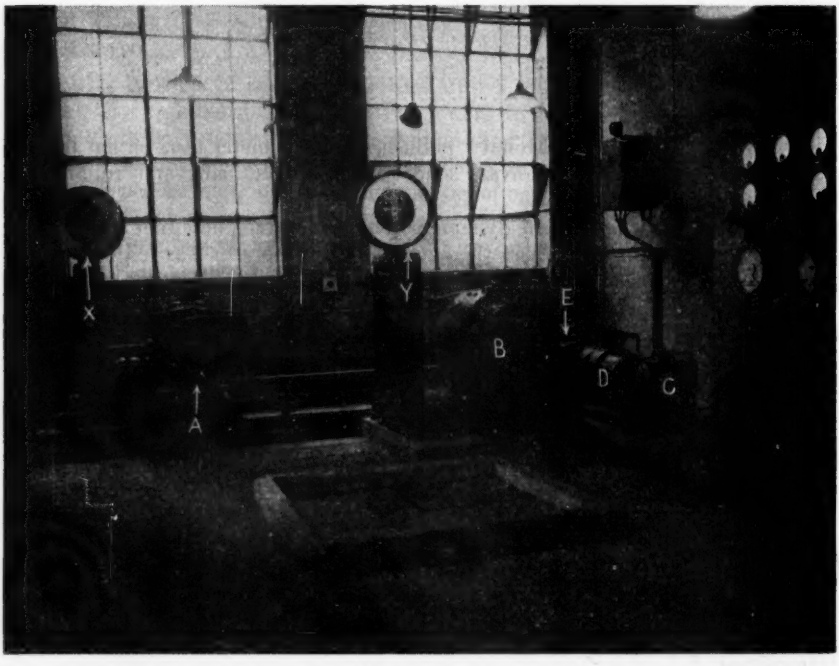

FIG. 1.—General view of dynamometer excluding steelyard and exciter.

A Dynamometer motor.
B Dynamometer generator.
C 20 h. p. 3-phase motor.
D Booster.
E Main generator.
X Torque dial for motor A.
Y Torque dial for generator B.

A somewhat similar machine was used by Skane[6] to study the performance characteristics of a 4-inch × 4-ply rubber transmission belt, the work also including an investigation as to the effects produced by variation in pulley sizes. Skane found that the horse-power-slip curves of a rubber belt altered in character with an increase in the size of the pulleys and that the most economical sizes of pulley for a 4-inch × 4-ply belt ran from 12 inches to 18 inches in diameter.

Carpenter[7], in a series of articles in 1934, also described a typical form of dynamometer used by rubber manufacturers.

From the preceding review, it will be seen that although a considerable amount of work has been done at various times on the performance characteristics of

power-transmission belting and much data have been obtained as to its general fundamental properties, the work has been somewhat scattered and has dealt mainly with the behavior of leather belting. In addition, much of the work has been done on "proprietary" or special types of manufacturers' belting and very little work has actually been published by which a direct comparison of different kinds of flat belting or a comparison between these and typical belts of a V type could be made. The object of the present paper is, therefore, first, to give a description of an electrical type of dynamometer containing features which it is felt would be of interest and, secondly, to present data obtained on the machine of interest to engineers and users of belting generally.

For reasons which will be apparent the tests now surveyed have been confined to the actual running characteristics of belts used on open horizontal drives and do not include any examination of their behavior on other types of drive. The survey also does not include tests designed to estimate the ultimate life of the belt under any given working conditions.

DESCRIPTION OF DYNAMOMETER USED

A general view of the dynamometer used for these tests is shown in Figure 1. It consists essentially of a dynamometer-motor (A) and a dynamometer-generator (B) designed so that the power supplied to the belt undergoing test and the power delivered by the belt to the generator can be accurately measured. These two machines will subsequently be referred to as "motor A" and "generator B." The motor A is a 25 h.p. machine capable of full output between 500 r.p.m. and 1,500 r.p.m.; the available power below 500 r.p.m. being approximately proportional to the speed, a condition of constant maximum torque.

The generator B also develops the same maximum horse-power between speeds of 250 and 1,500 r.p.m., the maximum output again being approximately proportional to the speed when this is below 250 r.p.m. The generator B is mounted on a bedplate provided with lateral adjustment so that correct alignment of the belt can be ensured. The motor A is mounted on a practically frictionless carriage which can be moved along highly polished rails. It can, however, also be rigidly attached to the rails at any one position, which enables constant-center tests to be carried out up to a maximum center distance of 21 feet.

The maximum speed ratio of the machines at their full rated output is 6 to 1, which can be obtained with a 5-inch pulley on the motor running at 1,500 r.p.m. and a 30-inch pulley on the dynamo running at 250 r.p.m.

Normally, tension is applied to the carriage of motor A by means of a chain leading to an Avery steelyard, as shown in Figure 3 at (*e*). For ease of operation, this steelyard is mounted on an independent trolley, which is fixed to the rails near the carriage of motor A, but which can be moved to any desired position along the rails. By means of this machine and a motorized winch, mounted on the dynamometer motor carriage, tension can be applied by hand or automatic control, which thus enables tests to be carried out under constant tension and up to a maximum center distance of 21 feet. The automatic control of this tension winch permits the machine to be used for continuous and long-period tests without personal attention, under conditions whereby the total belt tension (T_1+T_2) is constant up to a maximum of 1,500 lbs. This control is obtained by the use of a relay switch actuated by the poise of the steelyard on the tension measuring machine.

The equipment employs the principle of the Hopkinson test machine, a closed

energy circuit being used, the electrical output from the generator B being fed back into the motor A. To achieve this, compensation for voltage differences between the two machines is provided by utilizing two smaller independent machines, a booster and a generator which will be referred to as the main generator. By the use of these two machines, under any given set of speed conditions, electrical equilibrium can be maintained, either by regulation of the voltage of the generator B, or if necessary, by connecting the booster in series with the generator B and adjusting the booster voltage as required from the control panel.

The main generator and booster are mounted on the same common shaft and are driven by a 20 h.p. squirrel-cage a.c. motor, running at 1,450 r.p.m. This

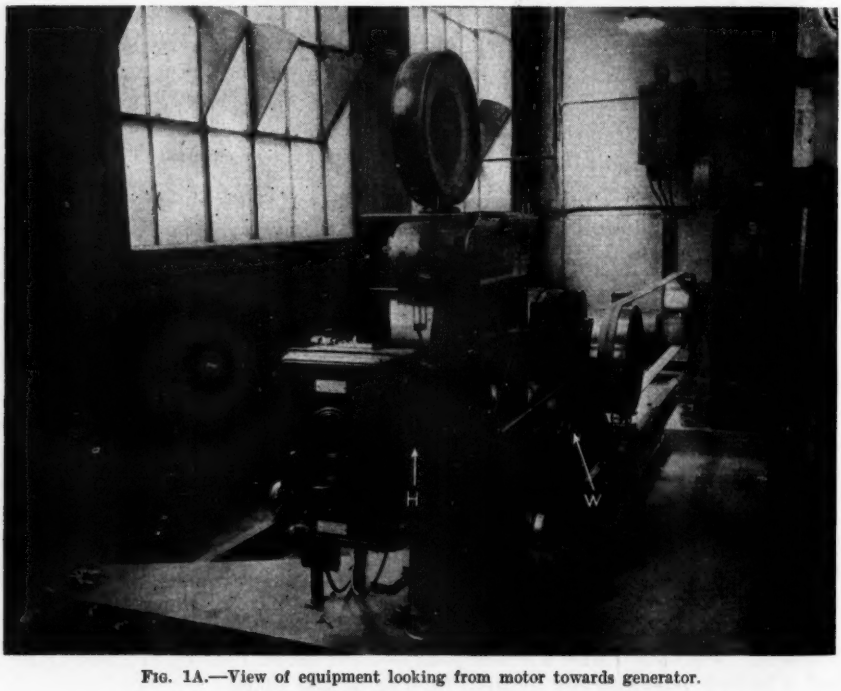

FIG. 1A.—View of equipment looking from motor towards generator.
A folded edge rubber-canvas belt is shown on test on 20 in. diam. pulleys.
In this view the overriding hand control H and switch gear operating W are clearly visible.

motor also drives a small exciter which excites the fields of the motor A, the generator B, as well as the fields of the booster and main generator. The general arrangements of these can be seen in Figure 1.

The performance of the booster is given by the following limiting values:

(*a*) +160 volts and 110 amps at 1,450 r.p.m.
(*b*) −180 volts and 40 amps at 1,450 r.p.m.

In the case of (*a*), the booster voltage augments that of the generator B, whereas when the booster voltage is negative as in (*b*), it can be considered as being driven by the generator B. In this way it gives mechanical assistance to the squirrel-cage a.c. motor in driving the main generator.

The casings of both machines A and B are mounted on large bearings con-

centric with the armature bearing so that the torque applied to the armature is measurable as an equal torque applied to the casing. The casings are prevented from rotating by means of the torque arms connected to Avery Toledo dead-beat weighing machines and in this way the torque in the system is measured. In order to measure the power which the belt is transmitting it is necessary only to multiply the observed generator B torque by the revolutions per minute of the shaft. The power supplied by the motor to the belt can also be measured at the motor in a similar way. For the purpose of performance tests on belting, however, it is not normally required to know the power which the belt is transmitting, but only (T_1+T_2) and (T_1-T_2), and of course with any given pulley size (T_1-T_2) is proportional to the torque which the belt is maintaining.

The "windage" of the machines has been counteracted by the use of suitable deflectors, which also take care of the windage of 20-inch flat pulleys when they are used, but a small correction is necessary for other pulley sizes. The torque dynamometers were used to determine the correct size of these deflectors.

Electrical tachometers have been fitted to measure the speeds of the dynamometer motor and the dynamometer generator. Total belt slip (including creep) is measured by means of a differential stroboscope, a divided scale fixed round the shaft of the generator B being illuminated by a neon lamp which is operated from a commutator contact on the shaft of the motor A.

The various controls, instruments and switchgear have been centralized on a control panel shown in the photograph in Figure 2. A brief description of these may be of interest.

A shunt field regulator is provided for each d.c. machine in the system, and these are marked with letters corresponding to the letters used in Figure 1 for the machines. Single-pole circuit breakers in the main generator—motor A circuit and in the generator B—main generator circuit are arranged to break at 150 amps. The electrical tachometers for motor A and generator B are clearly shown near the center of the panel. A knife switch, G, is used to short-circuit the booster if not required and another, H, to parallel the leads from the generator B on to the leads from the main generator to the motor A. Volt meters at V_1 and V_2 are provided so that the voltages of the exciter, the main generator and the motor A can be observed by means of a three-way switch; by the use of a four-way switch placed below V_2, the voltage of the booster, whether positive or negative, of the generator B, and of what is known as the change-over-switch, can be observed. This change-over switch is operated in order to feed the output of generator B (either with or without the booster D in series), in parallel with the main generator leads to the motor A, and it is obvious that for this the voltages must coincide.

Actually, for speeds below 1,000 r.p.m. the booster is not required. For higher speeds the booster is used in series with dynamometer generator B.

DISCUSSION OF RESULTS

The choice of any particular belt for any given drive will depend on a number of different characteristics which naturally must have relation to the special conditions and purpose of the drive. Although many factors may actually influence the ultimate choice, probably the two most important properties are frictional grip or pulling efficiency, otherwise called the performance characteristic, and ability to transmit power with the minimum of slip. Tests were therefore carried out on the machine just described to compare different types of belt

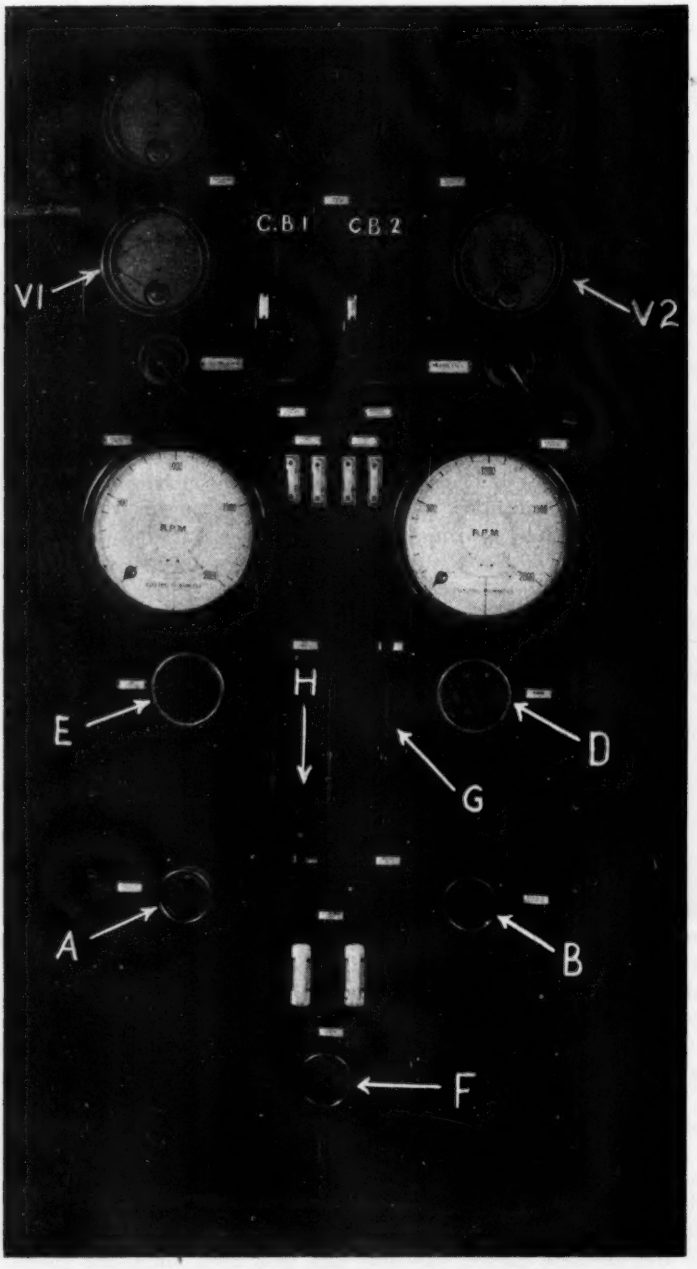

FIG. 2.—View of switchboard, showing controls and instruments.

from this point of view, the belts being made endless. The following represent the belts used:

1. Flat belts. 3 inches wide	Key to graphs
1. Solid woven, rubber-impregnated	W.R.
2. Folded-edge type, rubber and canvas, 4-ply, 28-ounce, soft type duck	F.R.
3. Square-edged rubber and canvas, 4-ply, 34-ounce hard type duck	S.E.
4. Square-edged, rubber and canvas belt, 3-ply, 34-ounce duck, with longitudinal cotton cord embedded in rubber as the face	C.F.
5. Folded-edge type, balata and canvas, 4-ply, 34-ounce duck.	B.
6. Good quality oak tanned leather, 5 mm. substance	
(*a*) Undressed	O.U.
(*b*) Dressed	O.D.
7. Good quality chrome tanned leather, 5 mm. substance	
(*a*) Undressed	C.U.
(*b*) Dressed	C.D.
2. V Belts, C Section	
8. V Belt rubber and cord, type 1	V.1.
9. V Belt rubber and cord, type 2	V.2.

The conditions of test were selected so as to eliminate as far as possible any factors which might be likely to influence the gripping properties of the belts. For the flat belts, a 20-ft. length was taken and tests were carried out under conditions of constant tension between pulleys irrespective of the center distance. It is realized that this may not actually represent the normal conditions of service, since most belt drives run at fixed centers. Constant-tension tests, however, do eliminate any variation in tension caused by belt stretch, and therefore ensure conditions which are directly comparable. They also enable T_1 to be obtained, and this is required for calculating the coefficient of performance value $\left(\frac{T_1-T_2}{T_1}\right)$. It should also be pointed out that constant-center tests would actually show up the belts having low stretch to better advantage, as the tests now described have confirmed the observation made by previous workers that the total tension increases with the power transmitted, at constant or fixed centers.

Tests were carried out so that the total tensions were 150, 200, 300, 400, 600 and 800 lbs. The pulleys used for the tests were 20 inches in the case of flat belts and 12 inches in diameter in the case of the V belts. The belts were run at a speed of 1,250 feet per minute to avoid the effects of centrifugal force, windage and hysteresis. That this was so was borne out by tests carried out on a number of the belts at double this speed.

All the rubber belts were tested in the undressed condition, and only in the case of leather belts was dressing applied. Before the readings were made, all belts were "run in" under the full recommended working load. In all cases the belts were run with the tight side underneath, and in the case of the leather belts with the flesh side to the pulley, as belts of English make were used.

The results obtained have been presented in graphical form in Figures 4 to 9 inclusive. As it was possible to balance the torque values at the motor A and generator B, which are proportional to the effective tension (T_1-T_2), the total loss of power in the drive at any torque was indicated by the loss of speed which represented the percentage slip. The term torque is subsequently used in this paper to indicate the effective pull of the belt, as this is proportional to the turning effort or torque transmitted from one pulley to the other. In the graphs,

therefore, percentage slip has been plotted against the effective tension. It will be noted that the steeper and higher the curve at any given total tension, the more efficient is the belt as a means of transmission of power as, judged from this point of view, slip or loss of speed is undesirable.

The conclusions which can be drawn from the test data may be summarized as follows:

(1) The balata belt and all the flat rubber belts transmit almost their maximum torque before appreciable slip commences, *i.e.*, they reach a point when the

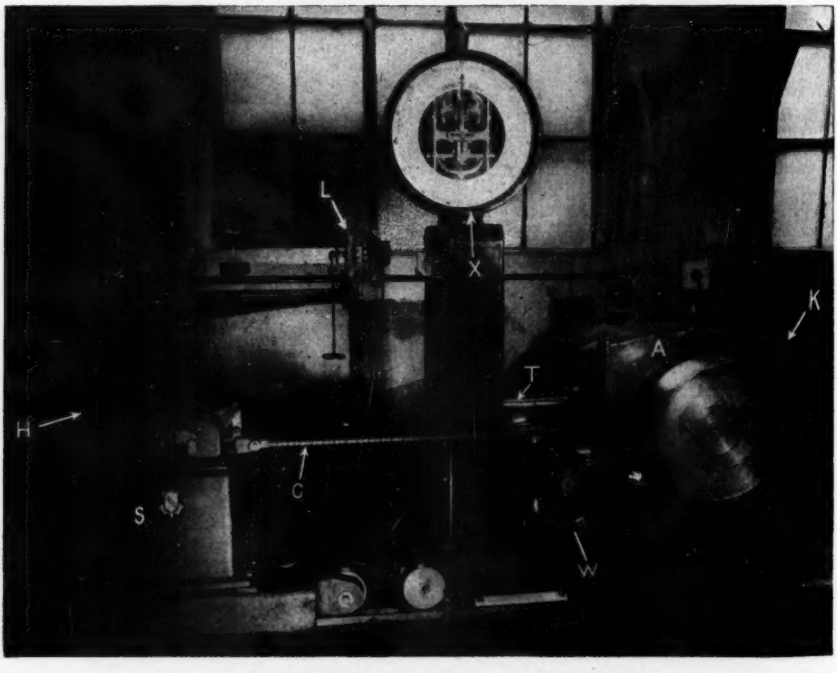

FIG. 3.—View of dynamometer motor and steelyard.

A Dynamometer motor (Mather and Platt).
X Avery Toledo dead-beat weighing machine for torque reaction measurement.
S Avery steelyard arranged to measure horizontal tension applied to carriage of motor A.
C Chain connecting A and S.
T Torque-arm connecting with X.
W Electrically-driven winch.
L Automatic contacts operating W.
H Overriding hand control operating W.
K Deflector for windage compensation.

rate of increase in slip rises suddenly, following which the torque transmitted is practically independent of slip. The leather belts, on the other hand, do not exhibit this tendency to reach maximum torque without appreciable slip, although after dressing they reach still higher torque values, with, however, a still more pronounced increase in slip. All belts other than leather screeched badly at the high loads when bodily slip was taking place.

From these observations it appears that rubber and balata belts are particularly suitable for industrial drives where a "safety valve" is required to prevent possible damage to machinery, *i.e.*, in case a drive becomes jammed or grossly overloaded. Also the screeching which accompanies slip would serve as an audible

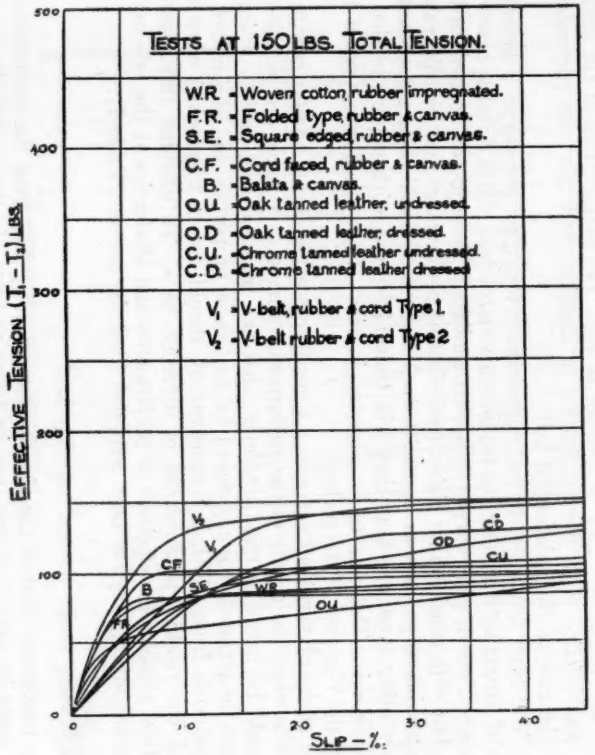
TESTS AT 150 LBS. TOTAL TENSION.
W.R. = Woven cotton rubber impregnated.
F.R. = Folded type rubber & canvas.
S.E. = Square edged rubber & canvas.
C.F. = Cord faced, rubber & canvas.
B. = Balata & canvas.
O.U. = Oak tanned leather, undressed.
O.D = Oak tanned leather, dressed.
C.U. = Chrome tanned leather undressed.
C.D. = Chrome tanned leather dressed
V1 = V-belt, rubber & cord Type 1.
V2 = V-belt rubber & cord Type 2
EFFECTIVE TENSION (T1 - T2) LBS.
SLIP - %.
0
100
200
300
400
500
1·0
2·0
3·0
4·0
V2
V1
CF
B
SE
FR
WR
OU
CD
OD
CU

Fig. 4.

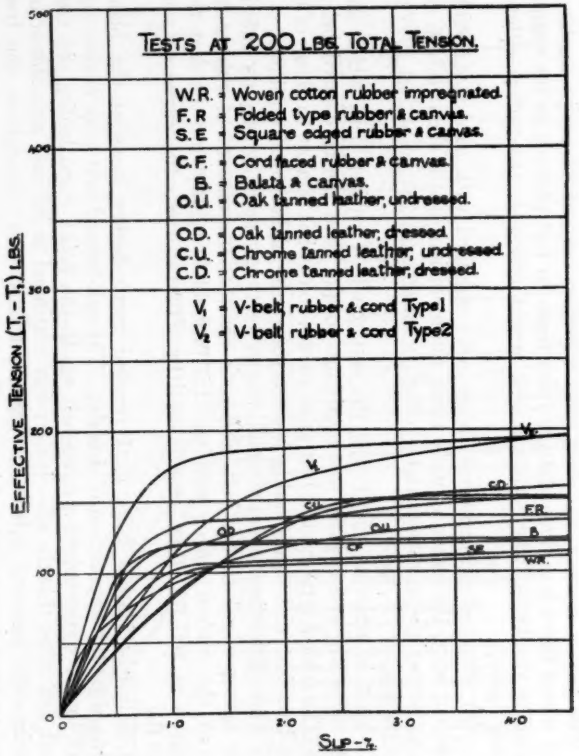
TESTS AT 200 LBS. TOTAL TENSION.
W.R. = Woven cotton rubber impregnated.
F.R = Folded type rubber & canvas.
S.E = Square edged rubber & canvas.
C.F. = Cord faced rubber & canvas.
B. = Balata & canvas.
O.U. = Oak tanned leather, undressed.
O.D. = Oak tanned leather, dressed.
C.U. = Chrome tanned leather, undressed.
C.D. = Chrome tanned leather, dressed.
V1 = V-belt, rubber & cord Type1
V2 = V-belt rubber & cord Type2
EFFECTIVE TENSION (T1 - T2) LBS.
SLIP - %
0
100
200
300
400
500
1·0
2·0
3·0
4·0
V2
V1
CD
CU
OD
CU
FR
B
CF
SE
WR

Fig. 5.

warning that the belt is being overloaded. A leather belt, on the other hand, would continue to pull harder while slipping excessively and would give no warning. The results however do show that a leather belt might be preferable on drives where there is sudden shifting from loose to fast pulleys, as for example on planing machines, where such a belt would still grip the pulley although slipping badly.

(2) (*a*) The best performance values were obtained with cord-faced rubber and balata belts, the latter actually being more efficient up to about 0.75% slip, but the former giving rather higher effective tensions at the point just previous to bodily slip.

(*b*) Next in order of merit was the square-edged rubber belt, which gave rather more slip and slightly less maximum torque than the cord-faced belt.

(*c*) The folded type rubber belt gave curves somewhat similar to those of the balata belt, but with considerably less torque at the higher total tensions.

(*d*) The rubber-impregnated solid woven belt was actually slightly inferior to the square-edged rubber belt, and as a considerable amount of rubber was worn off the surface during running, this probably accounts for the fact that the curve at 800 lbs. total tension is little different from the curve obtained at 600 lbs.

(*e*) Both the leather belts used reached much higher loads at the higher tensions after the application of dressing. The oak-tanned belt gave curves very similar to the square-edged rubber belt up to the point when bodily slip commenced, and after this the effective tension continued to increase at a slower but approximately constant rate. The chrome tanned belt, throughout the tests, showed an even greater rate of increase in slip. The performance of the leather belts was inferior until the application of dressing, and this was particularly so in the case of the oak-tanned belt.

(*f*) The type 2 V belt showed considerably less slip than Type 1 before a value of torque approaching the maximum was reached. Both V belts, however, especially Type 1, gave curves somewhat similar to those of the dressed leather belts, but with considerably higher coefficient of performance and less slip values when maximum power was transmitted. A feature of the V belts not possessed by any other type was that they will transmit torque without any tension in the slack side. This was to be expected in view of the wedging action of the belt in the V-groove of the pulley.

The above observations serve as a general indication of the relative merits of the belts when the results of the performance curves as a whole are considered. It should be borne in mind, however, that the practical safe load to which a belt can be stressed, having regard to its tensile properties and the nature of the materials from which it is constructed, should not be overlooked when assessing the relative performance of different belts. To examine this feature, therefore, a table of coefficients of performance and efficiencies at the safe working values for $T_1 - T_2$ has been compiled from the curves (Table I).

(3) *Efficiency under normal working load.*

The maximum value of the effective tension $(T_1 - T_2)$, from the recommendations made by manufacturers, can be taken as from 150 lbs. to 210 lbs. in the case of flat belts and 110 lbs. in the case of V belts. To determine the efficiency of the various belts under conditions of maximum normal load, therefore, the percentage of slip at 180 lbs. effective tension in the case of flat belts and 110 lbs. in the case of the two V belts has been tabulated, and by subtracting these

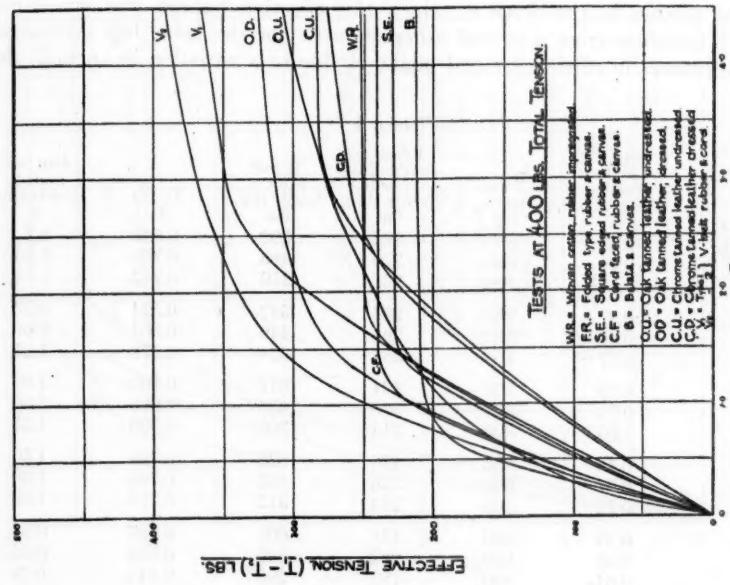
TESTS AT 400 LBS. TOTAL TENSION.
W.R. = Woven cotton rubber impregnated.
F.R. = Folded type, rubber & canvas.
S.E. = Square edged rubber & canvas.
C.F. = Cord faced rubber & canvas.
B. = Balata & canvas.
O.U. = Oak tanned leather, undressed.
O.D. = Oak tanned leather, dressed.
C.U. = Chrome tanned leather undressed
C.D. = Chrome tanned leather dressed
V1, V2 = V-belts rubber & cord
V1
V2
O.D.
O.U.
C.U.
W.R.
S.E.
B.
C.D.
C.F.
EFFECTIVE TENSION (T1 - T2) LBS.
SLIP-%

FIG. 7.

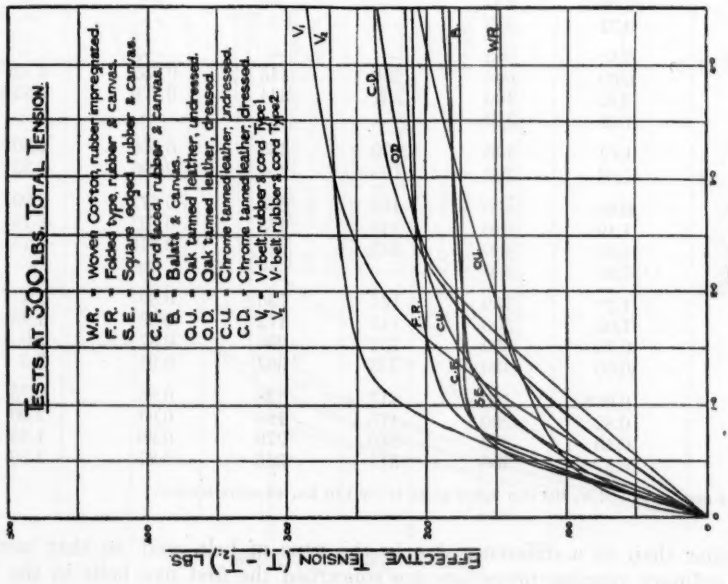
TESTS AT 300 LBS. TOTAL TENSION.
W.R. = Woven Cotton, rubber impregnated.
F.R. = Folded type, rubber & canvas.
S.E. = Square edged rubber & canvas.
C.F. = Cord faced, rubber & canvas.
B. = Balata & canvas.
O.U. = Oak tanned leather, undressed.
O.D. = Oak tanned leather, dressed.
C.U. = Chrome tanned leather, undressed.
C.D. = Chrome tanned leather, dressed.
V1 = V-belt rubber & cord Type1
V2 = V-belt rubber & cord Type2.
V1
V2
C.D.
O.D.
F.R.
C.U.
O.U.
C.F.
S.E.
B.
W.R.
EFFECTIVE TENSION (T1 - T2) LBS.
SLIP-%

FIG. 6.

figures from 100% a theoretical figure for the percentage efficiency of the belt has been obtained, which is shown in the second column. The third column gives the total tension in the drive at which this effective tension was maintained. Table II therefore gives a second order of merit for the belts, but in this case small differences in efficiency noted might be due to a variation in an individual

TABLE I

Belt	Slip at 180 lbs. effective tension, %	Total tension, lbs.	Effective tension just prior to bodily slip, lbs.	T_1 just prior to bodily slip, lbs.	$\frac{T_1-T_2}{T_1}$	Slip just prior to bodily slip, %
W.R.	0.55	800	384	592	0.649	1.3
	0.74	600	370	485	0.763	1.63
	1.125	400	237	319	0.743	1.57
F.R.	0.37	800	284	542	0.524	0.73
	0.48	600	298	449	0.664	1.00
	0.67	400	255	328	0.778	1.25
S.E.	0.55	800	434	617	0.703	1.90
	0.70	600	300	450	0.666	1.50
	1.05	400	218	309	0.706	1.35
C.F.	0.45	800	458	629	0.728	1.50
	0.61	600	326	463	0.704	1.30
	0.75	400	224	312	0.718	1.05
B	0.35	800	418	609	0.686	0.93
	0.44	600	292	446	0.655	0.85
	0.64	400	191	296	0.645	0.73
O.U.	0.90	400	—	—	—	—
	0.32	300	—	—	—	—
O.D.	0.52	800	—	—	—	—
	0.60	600	290	445	0.652	1.125
	0.82	400	267	344	0.776	1.45
	1.59	300	—	—	—	—
C.U.	1.64	400	270	335	0.806	2.80
	1.99	300	199	250	0.796	2.32
C.D.	0.93	800	410	605	0.677	2.90
	1.19	600	346	473	0.732	2.75
	1.55	400	238	319	0.746	2.25
	1.90	300	—	—	—	—
V_1	1.2*	150	121	136	0.89	1.4
	1.02	200	143	172	0.83	1.45
	0.75	300	232	266	0.87	2.0
	0.60	400	333	367	0.91	2.5
V_2	0.66*	150	117	138	0.85	0.75
	0.42	200	176	188	0.94	1.00
	0.40	300	240	270	0.89	1.25
	0.37	400	311	356	0.87	1.50

* In the case of V_1 and V_2 the slip figure given is for 110 lbs. effective tension.

belt rather than to a difference due to the type of belt used, so that insofar as the ordinary running properties are concerned the first five belts in the list can be regarded as similar. From an examination of the curves, however, it will be seen that greater additional gripping properties are shown by some belts, *e.g.*, the cord faced belt, when the total tension is increased, in comparison with the behavior of other rubber or balata belts. The results given in this

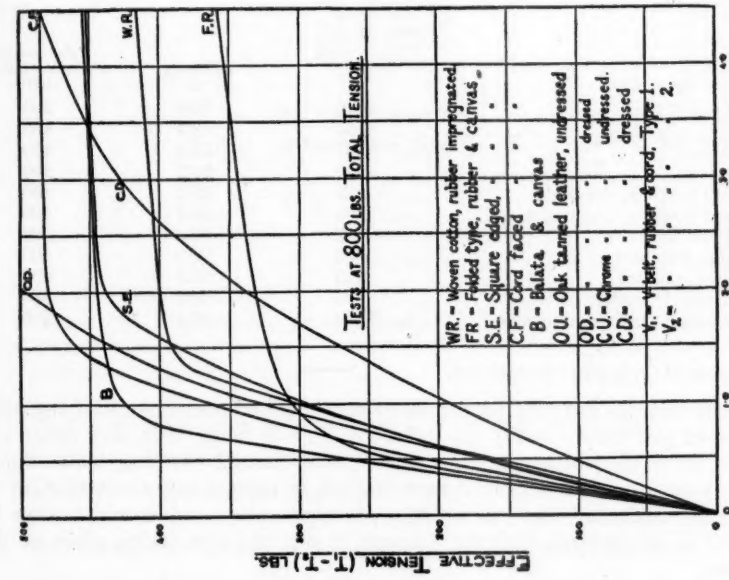
Tests at 800 lbs. Total Tension.
WR. - Woven cotton, rubber impregnated.
FR - Folded type, rubber & canvas.
S.E. - Square edged. " "
C.F. - Cord faced " "
B - Balata & canvas
OU. - Oak tanned leather, undressed
OD. - " dressed
CU. - Chrome " undressed.
CD. - " " dressed
V1 - V belt, rubber & cord, Type 1.
V2 - " " " 2.
Effective Tension (T1 - T2) lbs.
Slip - %.

Fig. 9.

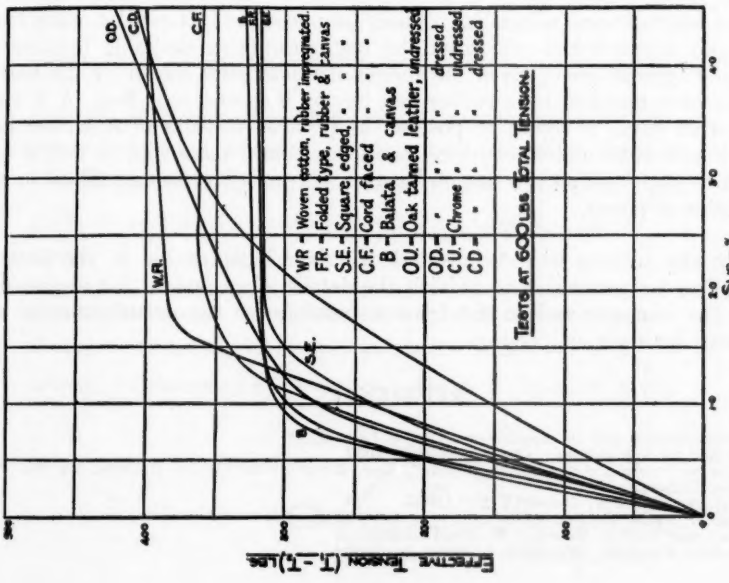
Tests at 600 lbs. Total Tension.
WR - Woven cotton, rubber impregnated.
FR. - Folded type, rubber & canvas
S.E. - Square edged. " "
C.F. - Cord faced " "
B - Balata & canvas
OU. - Oak tanned leather, undressed
OD. - " dressed
CU. - Chrome " undressed
CD - " " dressed
Effective Tension (T1 - T2) lbs.
Slip - %.

Fig. 8.

table, therefore, should be used in conjunction with the other data given in the paper and not considered separately.

TABLE II

Type of belt	Slip, %	Efficiency, %	Total tension during test, lbs
V Belt, Type 2	0.42	99.6	200
Balata	0.64	99.4	400
Folded rubber	0.67	99.3	400
Cord-faced	0.75	99.2	400
Oak-tanned leather, dressed	0.82	99.2	400
Oak-tanned leather, undressed	0.90	99.1	400
V Belt, Type 1	1.02	99.0	200
Square-edge rubber	1.05	98.9	400
Solid woven, rubber	1.13	98.9	400
Chrome-tanned leather, dressed	1.55	98.4	400
Chrome-tanned leather, undressed	1.64	98.4	400

(4) *Maximum gripping properties.*

If we consider the gripping properties or coefficient of performance of the belts at the point just before bodily slip takes place, it is found that they differ appreciably from the corresponding values under normal working load. Since, however, such a point is seldom if ever reached in normal use, the coefficient of performance, taken by itself, is of little practical value, and should always be considered in conjunction with the amount of slip which is taking place at the same time.

In conclusion, from a survey of the data given, it will be seen that, considered from the point of view of general running properties, a belt can be made from rubber and canvas which will meet the requirements or desirable features of almost any type of drive. Even the special characteristics shown by the balata belt have been matched by a rubber belt having a special cord face. A V belt, on the other hand, is shown to possess the peculiar features of a leather belt in that it will drive under conditions producing considerable slip, in fact it will continue to grip until all the tension between the pulleys is being utilized in the transmission of power.

Finally the authors wish to acknowledge their indebtedness to the Dunlop Rubber Co., for permission to publish the details given and to the engineering staff of the company and to the firms responsible for the manufacture of the equipment, for their coöperation.

REFERENCES

[1] Cited from "Belting and Its Applications", by J. Dawson, Jr.
[2] "Belting and Its Applications", Chapman & Hall, 1930.
[3] "Transmissive Power and Stretch of Belting", Eng. Experimental Station Bulletin, No. 41, Ohio State University.
[4] *Proc. Inst. Mech. Engrs.*, (London), Nov. 1928.
[5] *India Rubber World* 83, Dec. 1930, p. 68.
[6] *Proc. Am. Soc. Testing Materials* 30, Pt. II (1930).
[7] *India Rubber World* 91, Dec. 1934, p. 38.

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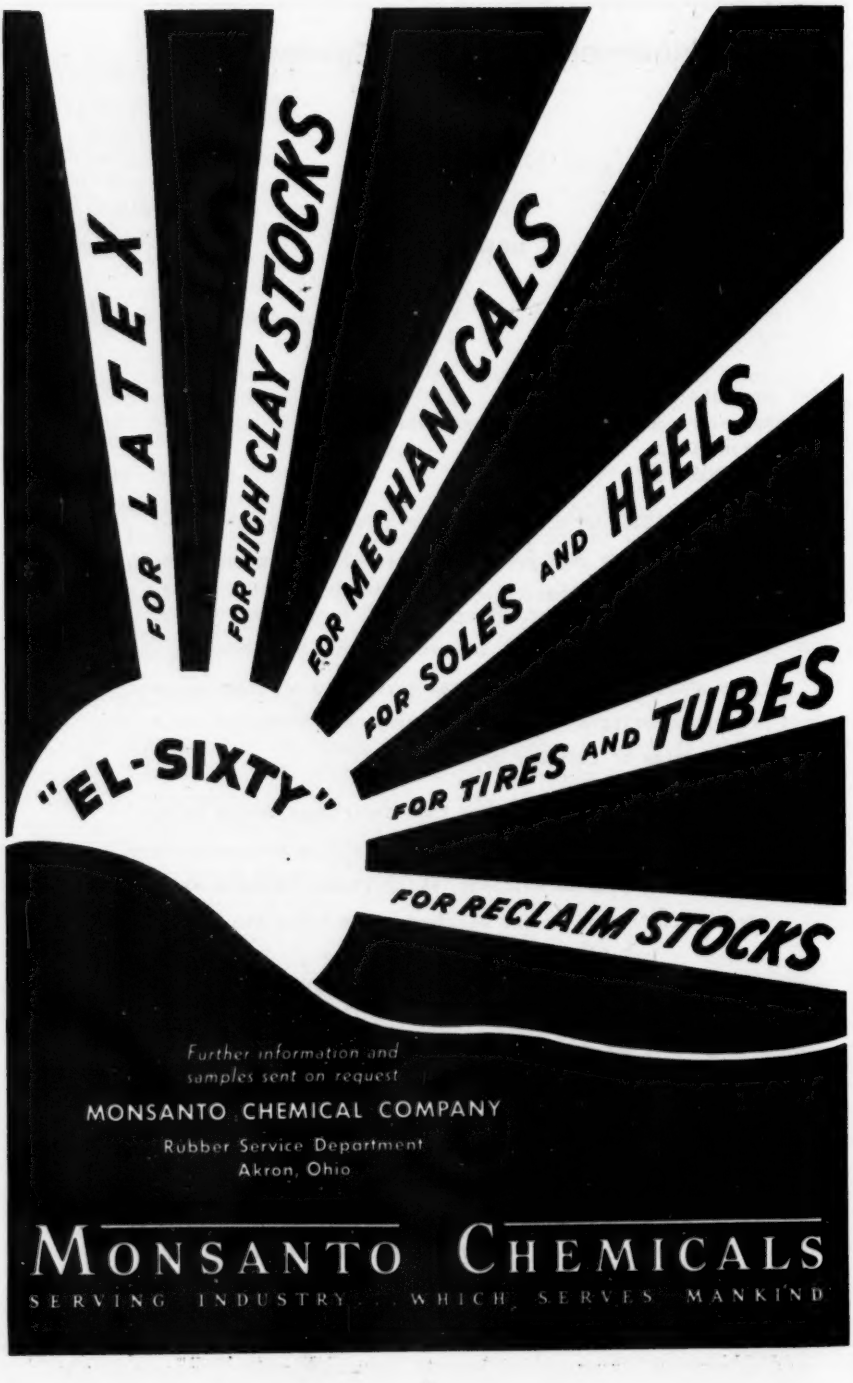
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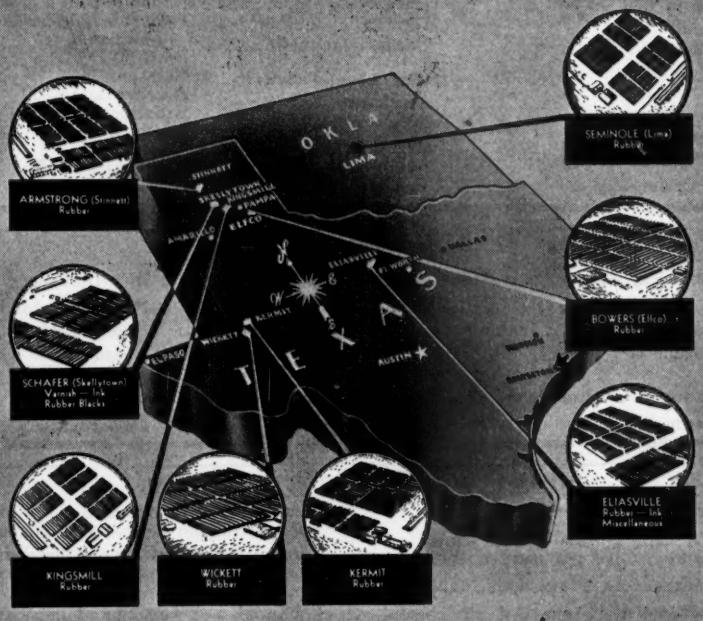

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